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AD 516 837

Final Report

March 1, 1970 to June 1, 1971

AFRPL-TR-71-93

August 1, 1971

**SYNTHESIS OF THERMALLY STABLE HIGH
DENSITY AND HIGH ENERGY PLASTICIZERS (U)**

By: D. L. ROSS, J. M. GUIMONT, M. W. LEROM, et al.

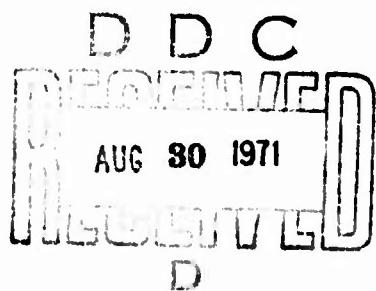
Prepared for:

AIR FORCE ROCKET PROPULSION LABORATORY
EDWARDS AIR FORCE BASE, CALIFORNIA 93523

Attention: MKPC

CONTRACT F04611-70-C-0037

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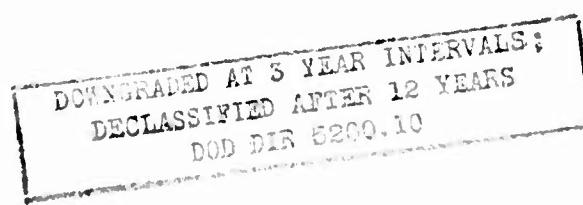
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FOREWORD (U)

(U) This final report was prepared by Stanford Research Institute, Menlo Park, California, for the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The report covers work carried over from March 1, 1970 to June 1, 1971 under Air Force Contract FO4611-70-C-0037. Scientists who contributed to the program include M. E. Hill, project supervisor, D. L. Ross, project leader, J. M. Guimont, M. W. Lerom, C. S. Nelson, and D. Tegg. Nmr analyses were performed by H. C. Barrett, and elemental analyses were performed by E. M. McCarthy.

(U) The AFRPL Contract Monitors were Capt. Paul Jendrek (MKPC) and Dr. Frank Roberto (MKPC).

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CONFIDENTIAL ABSTRACT (U)

(C) The primary objective of this research program was the synthesis of thermally stable, high density, and high energy plasticizers for new high energy polyether binders of interest to the Air Force. Initially the synthesis of three specific nitrodifluoramino-ether plasticizers was studied, but difficulties in synthesis and poor yields made their preparation impractical. The research effort was then redirected toward the synthesis of a series of nitrodifluoramino-formal plasticizers which resulted in the synthesis of SYFO, bis[5-fluoro-5,5-dinitro-2,2-bis(difluoramino)pentyl] formal. In overall properties, SYFO has outperformed all other energetic plasticizers known. Results of tests to date show that SYFO has the required high energy and density, low volatility, and thermal and chemical stability. In addition, SYFO imparts excellent properties to propellants formulated with it, and results in thermally stable propellants which heretofore have not been possible. A summary of work performed on this contract follows in order of performance.

(C) TDFH, 1,7-difluoro-1,1,7,7-tetranitro-4,4-bis(difluoramino)-heptane, which was discovered on a previous Navy contract, was prepared in larger quantities and submitted to AFRPL for evaluation as a plasticizer for P-GFDNE, and for PCDE. TDFH was found to be a very good plasticizer for these binders during formulation, but after curing, the propellant became brittle. This was probably due to a low degree of association between TDFH and other ingredients or the fact that a lower eutectic point was not achieved at the concentration of TDFH used.

(C) Nitrodifluoramino ethers were studied in order to obtain plasticizers similar in structure to TDFH but lower melting. Compounds studied included Goal Compounds I, IA, and II:

(C) Compound I, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$. Two synthetic approaches to Compound I were investigated. The first involved the addition of fluorodinitroethanol to epoxybutene. The reaction was

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carried out in base, but the epoxide opening was catalyzed by the acidic alcohol, fluorodinitroethanol, rather than the base. The resulting product was the undesired isomer. A second approach to the synthesis utilized a metathetical reaction between fluorodinitromethane and iodobutene. The desired product was obtained, but the yield was never greater than 5%.

(C) Compound IA, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{F}$. The synthesis of Compound IA was partially completed. Fluorodinitroepoxybutane was prepared by a metathetical reaction between fluorodinitromethane and allyl bromide followed by epoxidation with perrifluoroacetic acid. However, the reaction between fluorodinitroepoxybutane and fluorodinitroethanol always led to polymerization of the epoxide.

(C) Compound II, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$. Numerous approaches to the synthesis of Compound II were investigated. Only one gave any degree of success. The intermediate secondary alcohol



was prepared by the reaction of GFDNE with fluorodinitroethanol, but the yield was less than 1%. This and other routes were studied and found to be impractical for plasticizer synthesis.

(C) Nitrodifluoramino formals were proposed and studied since the physical properties expected of Compounds I, IA, and II could be achieved with the formals without loss of energy, and because the formals could be prepared with much less difficulty and in higher yield than the ethers.

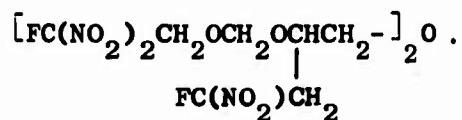
(C) The synthesis of each of six formals proposed involved the reaction of a nitrodifluoramino alcohol with the chloromethyl ether of fluorodinitroethanol or dinitropropanol. Three of the formals were prepared but their densities were low. An observation made during the preparation of one of the formals, FYOF, led to the synthesis of the symmetrical formal, bis[5-fluoro-5,dinitro-2,2-bis(difluoramino)pentyl] formal, SYFO. Our preliminary tests on the compound were encouraging; therefore a sample was prepared and submitted to AFRPL for further tests.

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Their results showed that SYFO was the best plasticizer tested to date. Because of the interest shown in SYFO, we have conducted a preliminary investigation of scale-up procedures for the preparation of pound quantities. At the present time it appears that the reactions can be scaled up to prepare several pounds of SYFO for motor firings. This work will resume in the near future.

(C) Fluoronitroethers were investigated briefly and synthesis achieved of DIAD, 1,15-difluoro-1,1,15,15-tetranitro-6,10-bis(2-fluoro-2,2-dinitroethyl)-3,5,8,11,13-pentaoxapentadecane,



This compound appears to meet all of the plasticizer requirements; however, it is not as energetic as SYFO. Additional work on DIAD was postponed in preference to work on SYFO.

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DIAD	1,15-Difluoro-1,1,15,15-tetranitro-6,10-bis(2-fluoro-2,2-dinitroethyl)-3,5,8,11,13-pentaoxapentadecane
Difluoro-FEFO	Bis(2-fluoro-2,2-dinitroethyl)difluoro Formal
EB	3,4-Epoxy-1-butene
FDM	Fluorodinitromethane
FDNE	2-Fluoro-2,2-dinitroethanol
FEFO	Bis(2-fluoro-2,2-dinitroethyl) Formal
FTM	Fluorotrinitromethane
FYOF	4,4-Bis(difluoramino)-1,10-difluoro-1,1,10,10-tetranitro-6,8-dioxadecane
FYOX	4,4-Bis(difluoramino)-1-fluoro-1,1,10,10-tetranitro-6,8-dioxaundecane
GFDNE	Glycidyl 2-Fluoro-2,2-dinitroethyl Ether
NC	Nitrocellulose
PCDE	Poly[cyano-difluoraminoethyl]ether
PGFDNE	Poly[glycidyl-fluorodinitroethyl]ether
SYFO	Bis[5-fluoro-5,5-dinitro-2,2-bis(difluoramino)pentyl] Formal
TDFH	1,7-Difluoro-1,1,7,7-tetranitro-4,4-bis(difluoramino)-heptane
TEGDN	Triethyleneglycol Dinitrate
TVOPA	1,2,3-Tris[1,2-bis(difluoramino)ethoxy]propane
XYOF	5,5-Bis(difluoramino)-11-fluoro-2,2,11,11-tetranitro-7,9-dioxaundecane
XYOX	5,5-Bis(difluoramino)-2,2,11,11-tetranitro-7,9-dioxadodecane
YXOF	2,2-Bis(difluoramino)-11-fluoro-5,5,11,11-tetranitro-7,9-dioxaundecane
YXOX	2,2-Bis(difluoramino)-5,5,11,11-tetranitro-7,9-dioxadodecane

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I INTRODUCTION (C)

(C) Thermally stable, high energy, and high density plasticizers are needed for use in propellants that will be subjected to extreme environmental conditions. The required binders for these propellants, PGFDNE and PCDE, appear to have been achieved, and have been undergoing evaluation by the Air Force. However, until the present research program was begun, no known plasticizers for PGFDNE and PCDE met all of the requirements. FEFO approached the requirements as a plasticizer, but was too volatile and lacked the desired energy. TVOPA had the required energy and low volatility but lacked the desired chemical and thermal stability. TDFH possessed the required energy, chemical and thermal stability, and high density; however, the compound was a solid melting at 53°C. TDFH was found to be a very good plasticizer for PGFDNE and PCDE during formulation, but after a period of time, the compound caused the propellant to become brittle--probably because of the crystallization of TDFH. It became obvious that, to achieve plasticization with retention of the propellant and chemical properties, a lower melting solid or high boiling liquid of low volatility and a structure similar to that of TDFH was required.

(C) The synthesis of Goal Compounds I, IA, and II, all ether analogs of TDFH, was proposed and investigated. These compounds contained the same energetic functional groups as TDFH, but they also contained ether groups which would tend to make them more liquid than TDFH. Later in the program, we found that none of the synthetic routes investigated was practical, even for the synthesis of small quantities for evaluation.

(C) The emphasis of the program was shifted to synthesis of the more readily prepared formals, compounds having the general structure ROCH_2OR in which R contains fluoro, nitro, and geminate-difluoramino groups. Several of these compounds were prepared, and the research culminated in the synthesis of SYFO, a compound which to date has met all

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(C) requirements as a plasticizer for the PCDE and PGFDNE binder systems.

After termination of the experimental work on this program, a sample of high purity SYFO submitted to AFRPL crystallized, and had a melting point of about 29°C. Nevertheless, propellants formulated with SYFO have continued to give results superior to any achieved heretofore.

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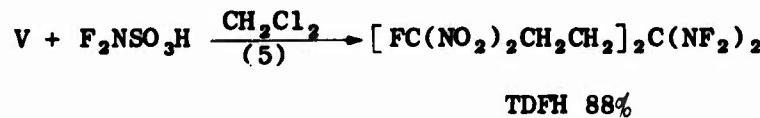
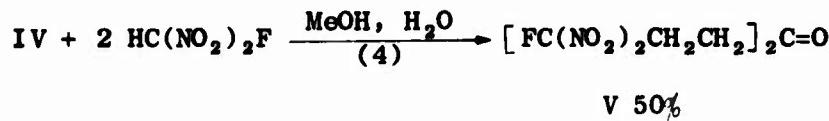
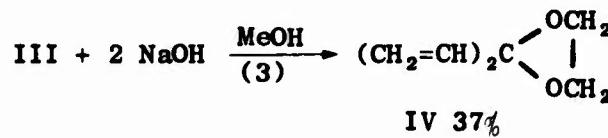
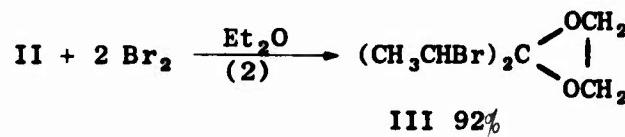
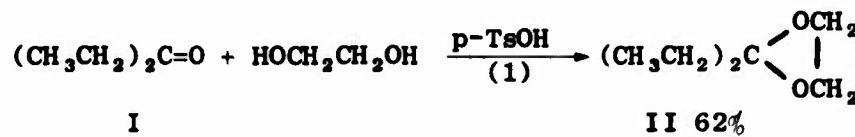
(C)

II DISCUSSION OF RESULTS (U)

A. Synthesis of 1,7-Difluoro-1,1,7,7-tetranitro-4,4-bis-(difluoramino)-heptane (TDFH) (C)

(C) TDFH was prepared under a previous Navy contract, and preliminary testing indicated that it was a very promising candidate plasticizer for double base systems. Because TDFH had the required thermal stability, density, energy, and nonvolatility, a sample was prepared and delivered to AFRPL for further investigation. The material is described as item C001 in Exhibit C of the subject contract.

(C) The synthesis of TDFH was carried out according to Eqs. (1-5) shown below; the average yield of each run is given.

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(C) The reactions shown in Eqs. (1-4) have been reported previously¹ as well as the reaction of Eq. (5).² During the course of work on the difluoroamination, Eq. (5), we found that it was not necessary to isolate TDFH in large quantities. The reaction mixture of Eq. (5) consisted of a sulfuric acid phase and a methylene chloride phase containing the desired TDFH. To remove impurities, the organic phase was washed with water, 5% sodium bicarbonate solution, and then with 6N sulfuric acid. After drying with MgSO₄, the organic phase was assayed for TDFH and its purity. Melting points were consistently 52-53°C. Aliquot samples of TDFH produced in this manner from each run were heated to 75°C overnight; the melted material remained clear and colorless, indicating highest possible purity. This factor would be significant if TDFH were to be produced on a larger scale. Time did not permit a long-term storage stability test on the TDFH in methylene chloride used for the reaction. To avoid possible decomposition on storage, the methylene chloride was removed and the TDFH was isolated in 10-g batches. This material was then redissolved in spectroquality methylene chloride for storage and shipment. A total of 110 g of TDFH was prepared; 108 g was shipped to AFRPL.

(C) During testing at AFRPL it was found difficult to formulate the propellant due to the high melting point of TDFH (54°C). TDFH also tended to crystallize out of the propellant after formulation; therefore work on TDFH was terminated, and research on its ether analogs begun.

B. Nitrodifluoramo Ethers (U)

(C) The synthesis of two ethers, Compounds I and II, was scheduled in the original contract, and later, Compound IA was investigated. Although the synthesis of each compound was partially completed, extremely low yields in all cases made continued work unrealistic.

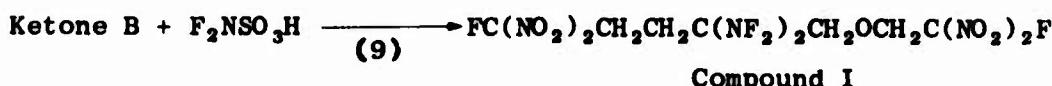
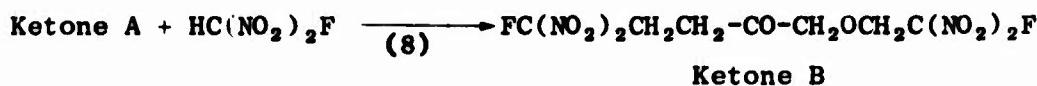
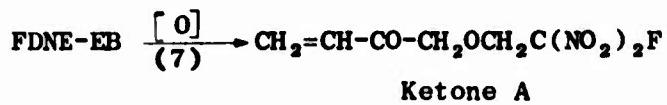
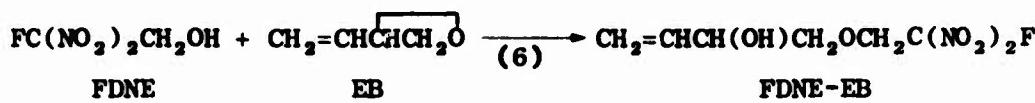
1. 1,8-Difluoro-1,1,8,8-tetranitro-4,4-bis(difluoramino)-6-oxaoctane (Compound I) (C)

(C) Compound I was proposed for synthesis because it contains the same energetic groups as TDFH but also an ether linkage which would tend to make it lower melting than TDFH. Since TDFH meets all of the requirements of a plasticizer for the composite system except for its high melting point, this compound appeared to be very promising.

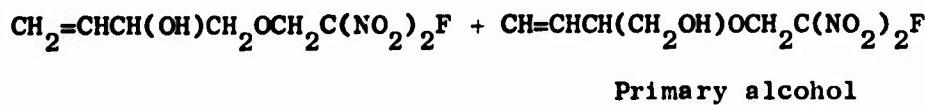
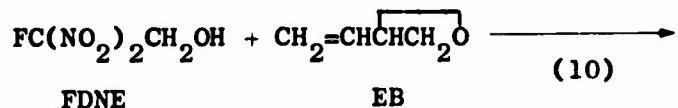
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(C) The reaction sequence, first proposed for the synthesis of Compound I is shown below.



(C) A series of reactions was run in which equivalent amounts of fluorodinitroethanol and epoxybutene were treated with different bases under several reaction conditions (see Table I). The reaction mixtures were analyzed periodically by glpc, but only Runs 2 and 5 showed any appreciable change. A high boiling product was isolated from Run 2, and the nmr, ir, and elemental analyses conformed to the desired product. However, two isomers are possible from this reaction: the secondary alcohol (FDNE-EB) and the primary alcohol, Eq. 10.



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Table I
 (C) REACTION OF FLUORODINITROETHANOL
 WITH EPOXYBUTENE (U)

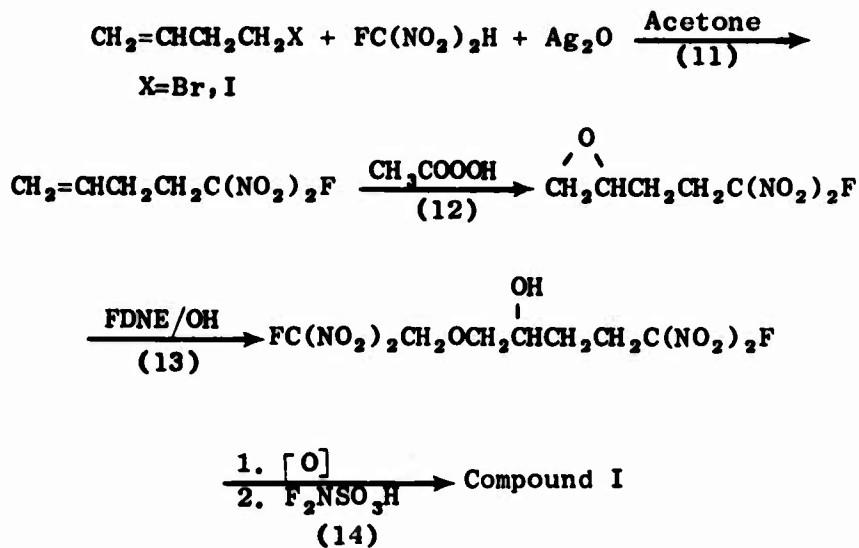
Run	Equiv FDNE	Equiv EB	Equiv Base	Temp, °C	Time, Days	Results
1	1	1	0.1	0-5	5	No reaction
2	1	1	1	0-5	5	Primary alcohol
3	1	1	0.1	25	5	No reaction
4	1	1	0.1	25	5	No reaction
5	1	1	2	0-5	4	Primary alcohol + 4% of secondary alcohol

(C) Nmr analysis of the isolated compound in CFCl_3 gave the following spectrum: δ 2.94 (s, 1, OH), 3.50 (d, 2, $\text{CH}_2\text{CH(OH)}$, $J = 4$ Hz), 3.95 (quadruplet or 2 overlapping triplets, 1, $\text{CH}(\text{OH})$, $J = 5.5$ Hz), 4.55 (pair of d, 2, CFCH_2 , $J = 18$ and 4 Hz), 5.5 (complex multiplet, 3, $\text{CH}=\text{CH}_2$). Since this spectrum did not distinguish FDNE-EB from the possible primary alcohol, the acetate ester derivative was prepared and analyzed by nmr. The nmr spectrum of the alcohol had a doublet for two protons at δ 3.50, which could be either $\text{CH}(\text{OH})\text{CH}_2\text{O}$ of the secondary alcohol or CH_2OH of the primary alcohol. Likewise, there was a quadruplet (two overlapped triplets) for one proton at δ 3.95, which could be either $\text{CH}(\text{OH})$ of the secondary alcohol or CHCH_2OH of the primary alcohol. If the alcohol were secondary, acetylation would cause the δ 3.95 quadruplet to be shifted downfield. However, the nmr of the acetate ester showed the δ 3.50 doublet to be shifted downfield to ca. δ 3.95-4.0; thus the parent alcohol was primary.

(C) Glpc analysis of Run 5, Table I, showed that two products were formed. One was the primary alcohol, and the other was identified as the secondary alcohol (FDNE-EB) by comparing an nmr of the mixture with the spectrum reported earlier by Grakauskas.³ Further attempts to improve the yield of secondary alcohol were not successful. Apparently FDNE is sufficiently acidic that regardless of how much excess base is in the reaction mixture, the epoxide opening is acid catalyzed and gives the primary alcohol almost exclusively.

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(C) Because the unexpectedly low yield of secondary alcohol made the original approach impractical, a second synthetic route was considered as follows, Eqs. (11-14).



(c) The metathetical reaction (Eq. (11)), was carried out with bromobutene in three experiments; however, the bromine was not sufficiently reactive, and the fluorodinitromethane was decomposed by silver oxide. When iodobutene was used, the desired product, 5-fluoro-5,5-dinitro-1-pentene, was recovered in 5% yield. A number of reaction conditions were tried, but the yield could not be improved. Further investigation did not, therefore, appear practical.

2. 1,7-Difluoro-1,1,7,7-tetranitro-3,3-bis(difluoramino)-5-oxaheptane
(Compound IA) (C)

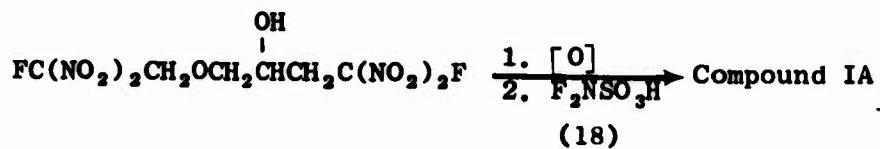
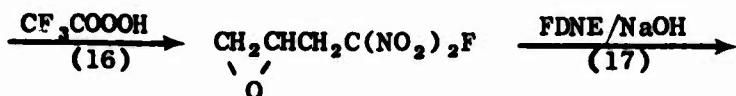
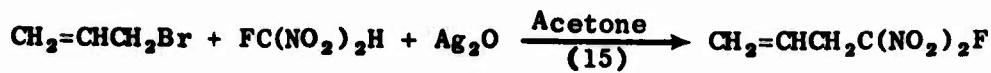
(C) When the synthesis of Compound I appeared impractical, we felt that a similar compound should be considered. Compound IA is the lower homolog and contains one less methylene group than Compound I.

(C) On another program we found that the reaction of allyl bromide, fluorodinitromethane, and silver oxide in acetone solution produced high yields of 4-fluoro-4,4-dinitro-1-butene. Because this compound is easily synthesized and readily available, it was considered a good candidate for an intermediate leading to a lower homolog of Compound I. The synthetic route to the homolog, Eqs. (15-18), is analogous to that given above for Compound I.

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(C)



After the epoxidation step, Eq. (16), the product was recovered in moderate yield and characterized by ir, nmr, and elemental analyses. The reaction of the epoxide with FDNE in aqueous NaOH, Eq. (17), gave 1.8 g of a clear, yellow, viscous oil which could not be distilled nor analyzed by glpc; it consisted primarily of polymerized fluorodinitroepoxybutane. The nmr spectrum of the material was very characteristic of a polymer and similar to that of P-GFDNE in that there was considerable broadening of the methylene signals.

3. 1,9-Difluoro-1,1,9,9-tetranitro-5,5-bis(difluoramino)-3,7-dioxanonane (Compound II) (C)

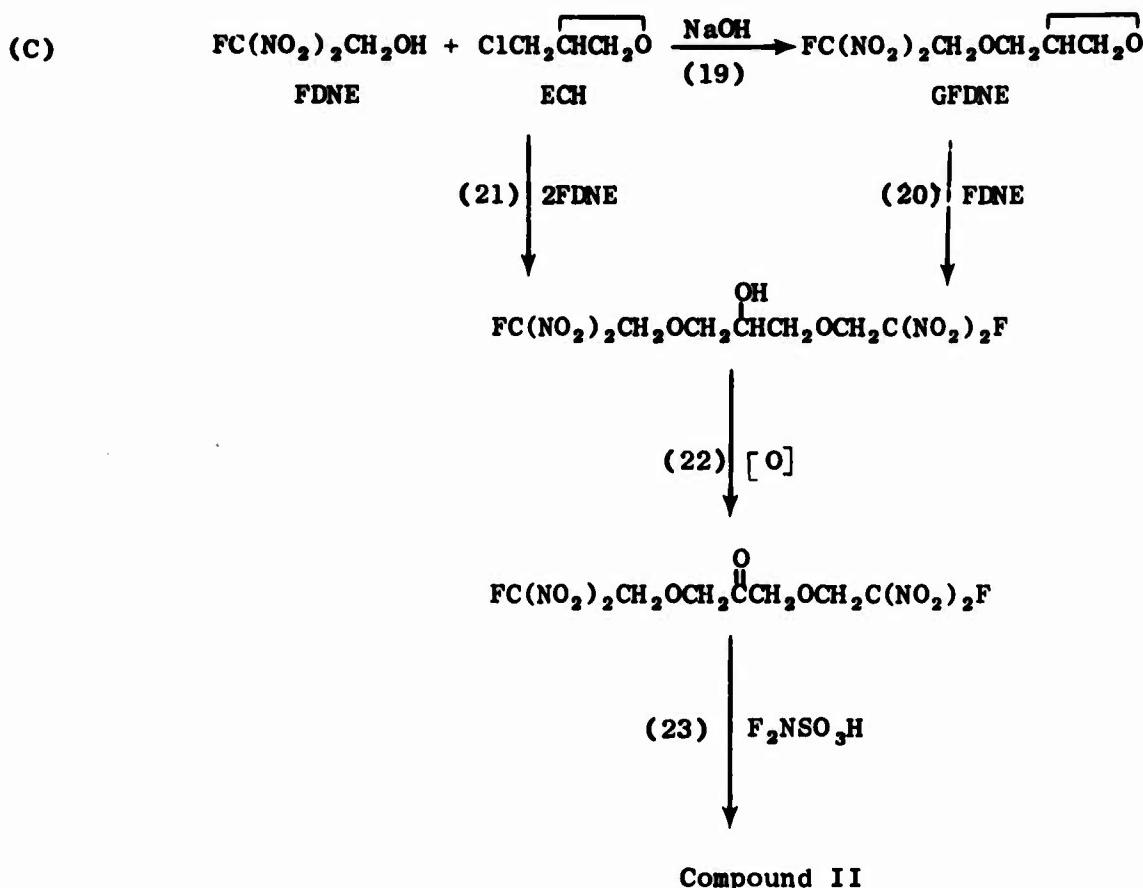
(C) Like Compound I, this compound was proposed because of its similarity to TDFH and because the ether group would tend to lower the melting point.

(C) Three synthetic routes for the preparation of Compound II were investigated. Although none was entirely successful, the alcohol intermediate, Eq. (20), was prepared in 0.6% yield by the procedure initially proposed. Because the yield could not be improved, we concluded the procedure was impractical even for the preparation of small amounts of Compound II. Hence, two other routes were investigated briefly, also without success.

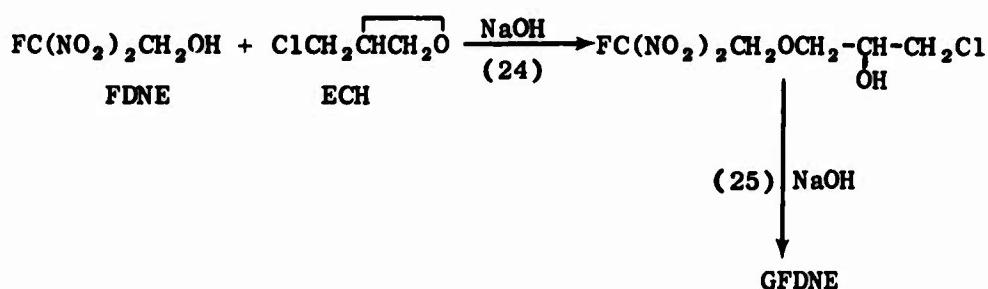
(C) The procedure first proposed is outlined in Eq. (19-23).

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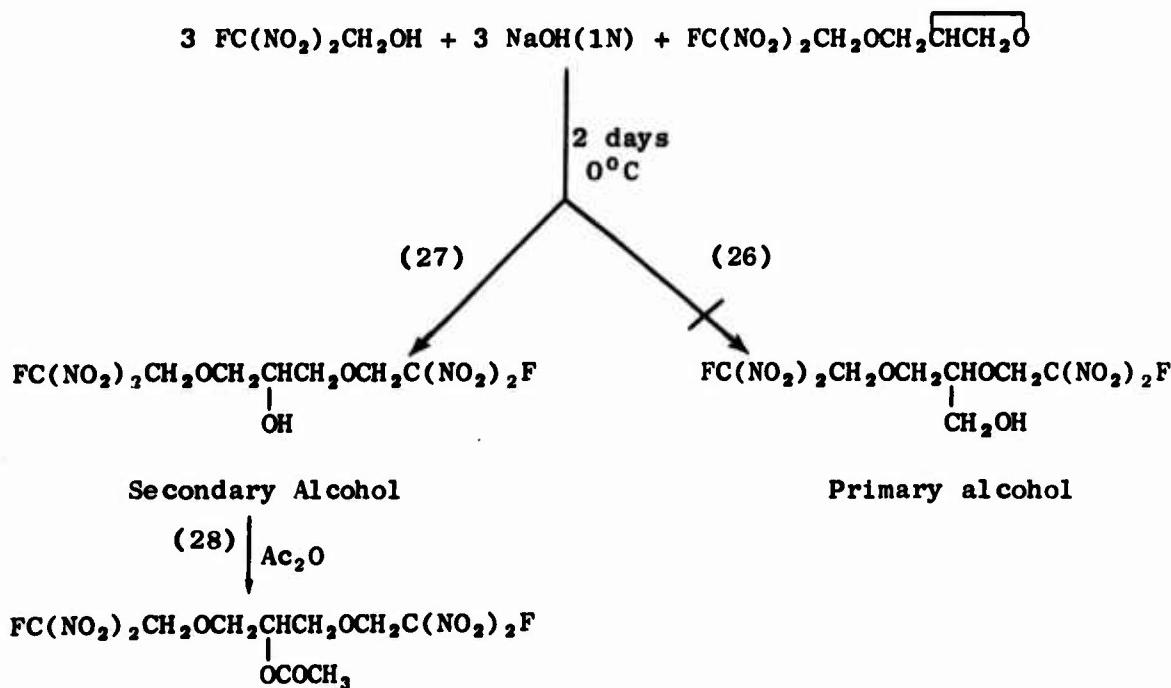
(C) GFDNE Eq. (19), was prepared in 15% yield by the method of Frankel³ using a two-phase reaction of FDNE with ECH and aqueous base. A by-product of this reaction was a chlorohydrin, an intermediate in the formation of GFDNE, Eq. (24). The chlorohydrin was characterized by ir and nmr analyses and by Beilstein's halogen test; in addition, treatment of the chlorohydrin with base gave GFDNE, Eq. (25).



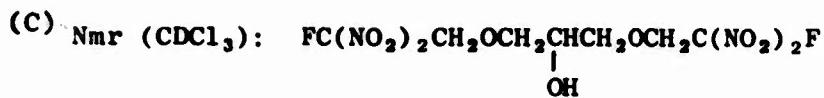
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(C) Initial attempts to prepare the secondary alcohol, Eq. (20), led only to recovery of starting materials and polymeric GFDNE. The only successful reaction was one in which a threefold excess of FDNE in 1N NaOH was allowed to stir with GFDNE for two days at 0°C. The organic materials from this reaction were extracted from the aqueous system and were fractionated by glpc using chloroform and silica gel. Fourteen fractions were collected and analyzed; fractions 1-7 contained GFDNE and FDNE, and fractions 8-14 contained only FDNE and a higher boiling alcohol. FDNE was evaporated from these latter fractions leaving 45 mg (0.6% yield) of a clear, colorless, mobile liquid that was identified by nmr as the desired secondary alcohol, Eq. (20). This alcohol could not be distilled nor analyzed by glpc.

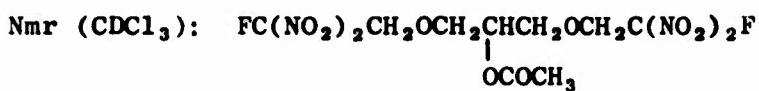
(C) There was a possibility that the primary alcohol, Eq. (26), had formed instead of the secondary alcohol, Eq. (27). If this were true, nmr analysis alone would not be sufficient to distinguish between the two. Therefore, we prepared the acetate of the alcohol, Eq. (28). The shift of the methyne proton multiplet, $\text{CH}(\text{OH})$, by 1 ppm downfield to give a distinct quintuplet showed that the alcohol was secondary and not primary. The acetate of the primary alcohol would have resulted in a downfield shift of the CH_2OH protons.



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<u>Shift, τ</u>	<u>Assignment</u>	<u>J, Hz</u>	<u>Area</u>
5.40 Doublet	FC(NO ₂) ₂ CH ₂ -	17	4
6.37 Doublet	-OCH ₂ -	3	
6.37 Multiplet	-CH(OH)-	5 }	5
7.69 Singlet	-OH	-	1



<u>Shift, τ</u>	<u>Assignment</u>	<u>J, Hz</u>	<u>Area</u>
5.44 Doublet	FC(NO ₂) ₂ CH ₂ -	17	4
6.26 Doublet	-OCH ₂ -	5	4
5.36 Quintuplet	-CH(OAc)-	5	1
7.93 Singlet	CH ₃ -	-	3

(C) Because of the extremely low yield of secondary alcohol, the preparation of Compound II by this method was not practical. However, based on the work of earlier investigators,⁴ the yield should have been much higher. We felt very strongly that the yield could be improved by varying solvents, catalysts, or reaction conditions.

(C) In reviewing previous base-catalyzed reactions of FDNE with epoxides, we found that only water had been used as the solvent. However, in these reactions, the starting epoxide (e.g. ethylene oxide, propylene oxide, epichlorohydrin) had always been water soluble.⁴ Therefore, the epoxide could easily react with fluorodinitroethoxide in the aqueous phase. In the case of GFDNE, the compound had no water solubility, and very little reaction could occur. Also, no reaction occurred when THF was used to solubilize GFDNE (also epichlorohydrin) for reaction with FDNE in aqueous base. Thus it appeared that, for reaction to occur, two

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(C)

requirements must be met: (1) the epoxide must be solubilized in water by some means, and (2) water and/or a hydroxylic solvent must be present in order to hydrate and stabilize the fluorodinitroethoxide anion. By using ethanol as a solvent, both of these requirements could be met.

(C) Three concurrent experiments were conducted in which varying ratios of GFDNE, FDNE, and NaOH in ethanol were allowed to react at 0-5°C for 15 hr. The mole equivalent ratios of FGDNE:FDNE:NaOH were 1:2:2, 1:2:1, and 1:1:1. Copious amounts of sodium nitrite separated from all three reaction mixtures, and we observed that the amount of sodium nitrite formed was directly proportional to the amount of sodium hydroxide used. The ethanol supernate from the three reactions contained starting materials, polymer, and a large amount of carbonyl-containing product that could not be separated or identified.

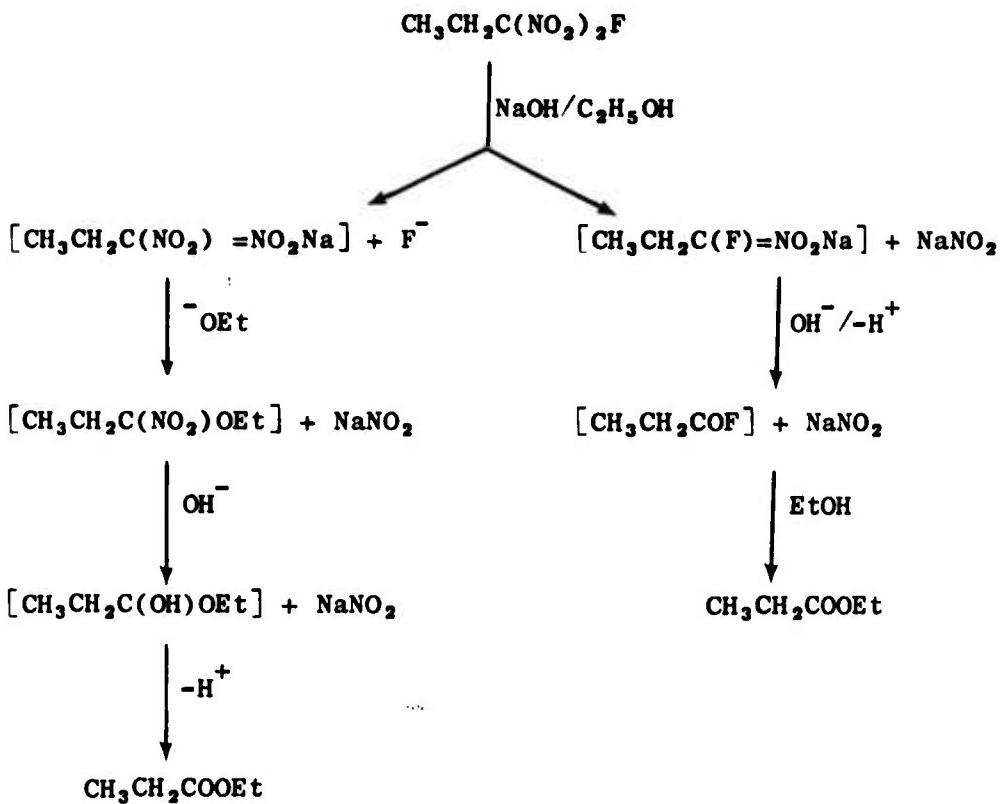
(C) In the above reactions, the formation of sodium nitrite could arise only from loss of nitrite from the fluorodinitromethyl group of either GFDNE or FDNE. At first glance it appears that FDNE would be less stable to base than GFDNE; therefore, we reasoned that the sodium nitrite and the carbonyl product of the reaction formed, as a result of deformylation of FDNE, into formaldehyde and sodium fluorodinitromethide. The latter is very unstable in base and thus its presence would account for the sodium nitrite formation. On the contrary, a GFDNE/NaOH/ethanol solution produced sodium nitrite in large amounts and much more than an FDNE/NaOH/ethanol solution.

(C) In order to determine the fate of the fluorodinitromethyl group in base, and still be able to identify its decomposition products readily, we treated fluorodinitropropane in ethanol with one equivalent of NaOH at 0-5°C. Sodium nitrite formed rapidly, and the major organic product identified was ethyl propionate. The proposed mode of product formation consistent with these results is shown in the equations below.

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(C)



(C) These results had a direct bearing on the reaction of GFDNE and FDNE in base which we had been conducting. In aqueous media we had always observed carbonyl-containing (ketone or carboxyl) products whose formation could not be accounted for by condensation of formadehyde. In addition, the carbonyl compounds were always extractable from other organic products with dilute base; therefore, they were no doubt carboxylic acids formed by base hydrolysis of the fluorodinitromethyl group. In addition to hydrolysis, polymerization has always occurred also. Therefore, in the reaction of GFDNE with FDNE to form the desired secondary alcohol, two known competing reactions are in effect. Depending upon the rates of these reactions, of course, only a finite yield of secondary alcohol can be obtained. These statements would also be true for the reaction of

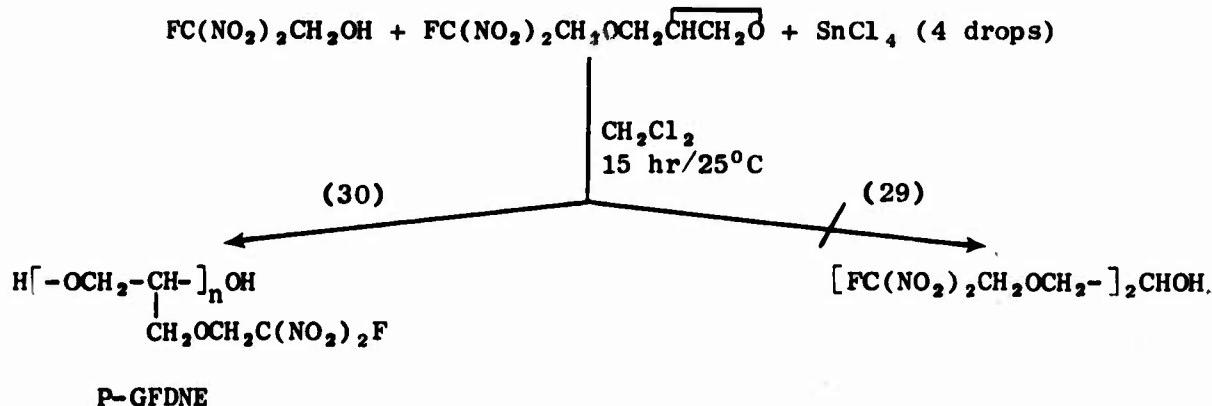
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FDNE with epichlorohydrin to give GFDNE; we find that no yields greater than 30% have been reported. In our experience, yields of GFDNE have been much less.

(C) In light of the above discussion, it appeared that the yield of secondary alcohol (0.6%) probably could never be improved significantly by using sodium hydroxide as a catalyst. A literature search showed that other catalysts have been used for the condensation of alcohols with epoxides. We felt that at least a brief investigation of each one was warranted.

(C) The stannic chloride-catalyzed reaction of FDNE and propylene oxide in methylene chloride solution was reported to give a 15% yield of $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3$.⁴ Lewis acid-catalyzed reactions of epoxides with alcohols are poor at best; polymerization of the epoxide is the usual course of reaction. Nevertheless, we attempted the analogous reaction of GFDNE and FDNE under the same conditions, Eq. (29).



(C) Some starting materials were recovered, but the reaction followed the usual course giving primarily P-GFDNE, Eq. (30).

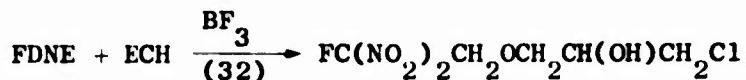
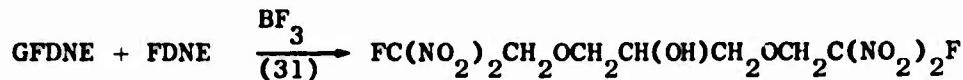
(C) Boron trifluoride (BF_3) catalyst was investigated briefly because it has been used successfully for numerous similar epoxide condensations.⁵ The reaction of GFDNE and FDNE with BF_3 catalyst, Eq. (31), in the cold and at 25°C for one to five days gave essentially polymers

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(C)

of GFDNE. To determine if BF_3 would indeed catalyze the desired ring opening, it was used in a reaction of FDNE and ECH which should have given the chlorohydrin, Eq. (32),



but in this reaction only polymer was formed and FDNE was recovered.

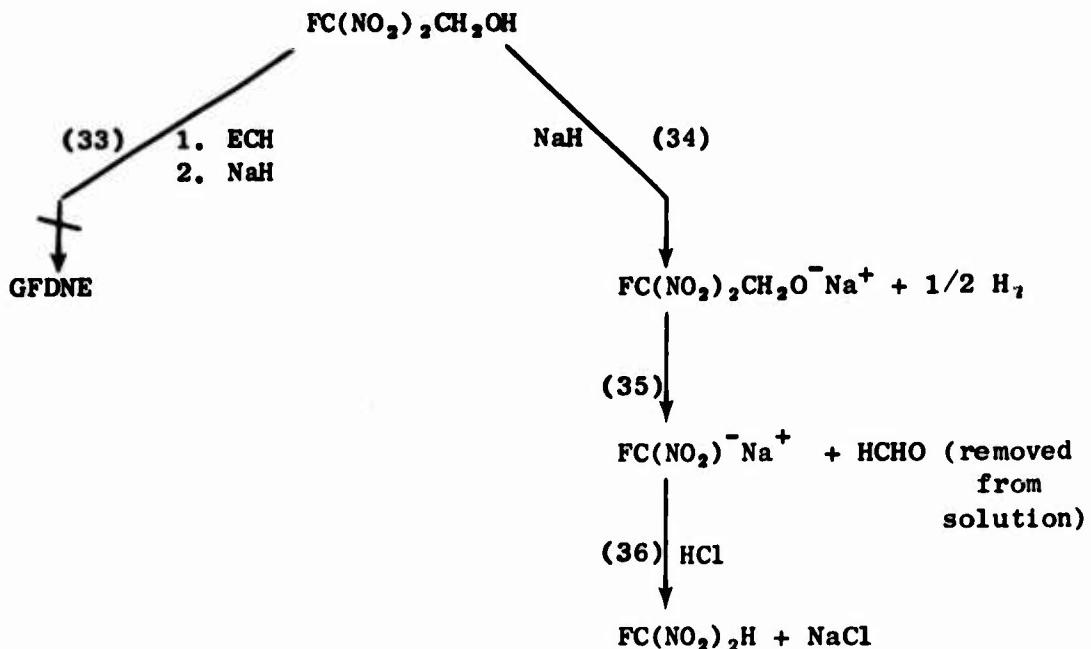
(C) Pyridine was also used as a catalyst for the reaction of GFDNE + FDNE, and FDNE + ECH. Experiments were carried out with neat reactants or with solvent (CH_2Cl_2) at ambient temperature with one equivalent of pyridine; and with neat reactants at 60°C with one-tenth equivalent of pyridine. With one equivalent of pyridine at ambient temperature, no reaction occurred. With one equivalent of pyridine at 60°C , decomposition occurred to give only tar products. With one-tenth equivalent of pyridine at 90°C , little or no reaction occurred and starting materials were recovered. But the fact that no chlorohydrin formed in any of the cases from reaction of FDNE + ECH showed that pyridine was not effective as a catalyst.

(C) Concurrent with the work described above, we also investigated other methods of obtaining high concentrations of the fluorodinitroethoxide anion for reaction with epoxides. A brief attempt was made to use sodium hydride as base instead of sodium hydroxide. Ether solutions of ECH and FDNE to which sodium hydroxide was added gave no GFDNE or its chlorohydrin, Eq. (33). A subsequent experiment was run in which an ether solution of FDNE was treated with NaH , Eq. (34). A yellow salt precipitated and was washed with ether and then resuspended in ether. The suspension was acidified with dry HCl , Eq. (36). The salt formed in this acidified mixture was filtered and shown to be sodium chloride. The filtrate was evaporated leaving fluorodinitromethane; therefore, the fluorodinitroethoxide anion, which no doubt formed, rapidly dissociated in the ether solution into

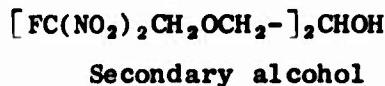
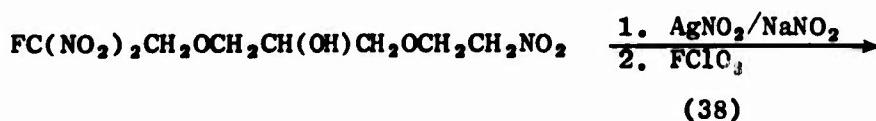
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(C) fluorodinitromethide and formaldehyde, Eq. (35). After removal of the formaldehyde, acidification produced fluorodinitromethane. The above discussion is summarized by the following equations.

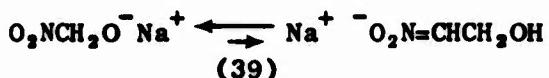


(C) In a final attempt to prepare the secondary alcohol from GFDNE, a brief study was made on the reaction of nitroethanol and also its sodium salt with GFDNE as proposed below, Eqs. (37-38).



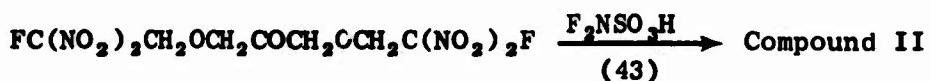
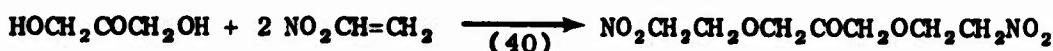
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(C) The nitroethoxide anion rather than aci-nitroethanol is reported to be the predominant species present in basic alcoholic and aqueous solutions, Eq. (39).



Therefore, reaction of the alkoxide with GFDNE should have readily occurred. We found, however, that use of either freshly prepared sodium nitroethoxide or sodium nitroethoxide prepared in situ gave the same results in aqueous or alcoholic solutions--hydrolysis of the fluorodinitromethyl group of GFDNE. Although the nitroethoxide did not produce as basic a medium as the sodium hydroxide used earlier, the solution was still sufficiently basic to cause hydrolysis of the fluorodinitromethyl groups.

(C) Because of the limited success of the reaction sequence using GFDNE, a second approach was attempted. The synthetic route is outlined in Eqs. (40-43), which are analogous to those described previously for Compound I.



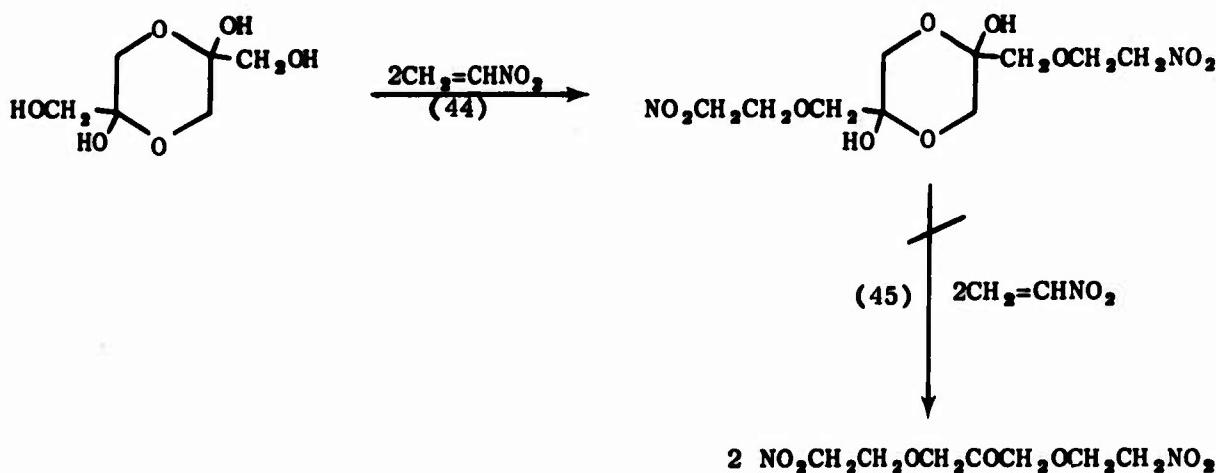
Nitroethylene was allowed to react with dihydroxyacetone under the following conditions:

- a) Dihydroxyacetone in nitroethylene as solvent at 85-90°C for 3 hr
- b) Dihydroxyacetone and 2.1 equivalents of nitroethylene in cyclohexanone at 85-90°C for 2 hr
- c) Dihydroxyacetone and 2.1 equivalents of nitroethylene in dioxane at 85-90°C for 2-4 hr.

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(C) Under these conditions no carbonyl-containing product was obtained from the reactions; the nitroethylene evidently reacted with dihydroxyacetone, Eq. (44), but not sufficiently to open the ring of the dihydroxyacetone dimeride which formed under the reaction conditions, Eq. (45).



(C) To prevent dimeride formation, the diethyl ketal of dihydroxyacetone was prepared⁷ and treated with nitroethylene under neutral and basic conditions, Eq. (46), Table II.

(C) The results of the reactions given in Table II showed that, above 70-80°C, the ketal decomposed and caused polymerization of the nitroethylene;⁸ the ketal alone slowly decomposed above 70-80°C. Below 70°C the ketal was partially hydrolyzed to give a ketone and polymer. Under basic conditions, polymerization occurred in preference to the desired reaction.

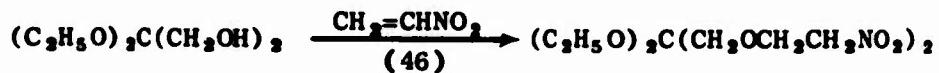
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(C)

Table II

(C) REACTION OF NITROETHYLENE WITH DIHYDROXYACETONE DIETHYL KETAL (U)



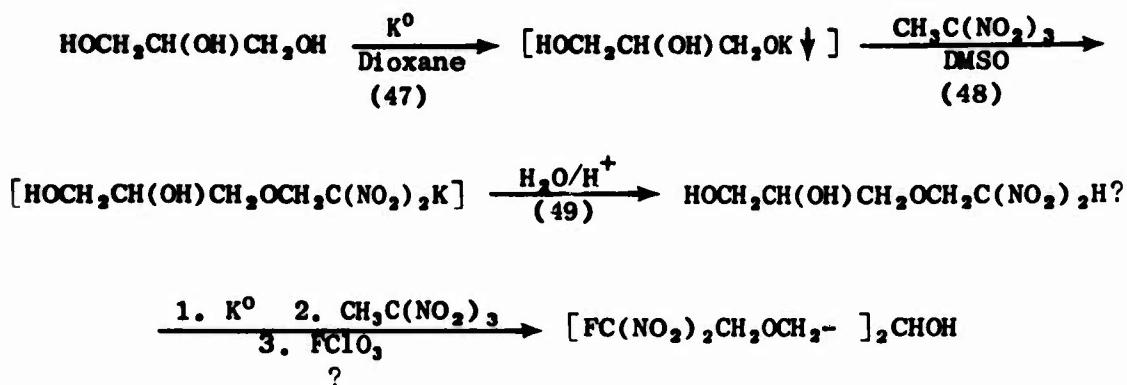
<u>Ketal,</u> <u>mmol</u>	<u>Nitroethylene,</u> <u>mmol</u>	<u>Solvent</u>	<u>Time,</u> <u>hr</u>	<u>Temp,</u> <u>°C</u>	<u>Results</u>
1.0	2.1	None	2	80	Polymer. Ketal decomposed.
1.0	2.1	None	6	70	Polymer. Ketal decomposed.
1.0	2.1	CHCl ₃	15	61	Polymer + starting material + ketone.
1.8	10.0	Nitro- ethylene	60	25	N.R.
1.0	2.1	CDCl ₃	55	40	Polymer + starting material + ketone.
1.0 ⁹	2.1	THF	6	0-25	Polymer.

(C) Since none of the above reactions gave any indication that the desired product could be obtained without great difficulty and a large investment of time, this work was discontinued in preference to a third approach to the synthesis of Compound II. The reaction sequence is outlined in Eqs. (47-49). The first three reactions were investigated and partially completed.

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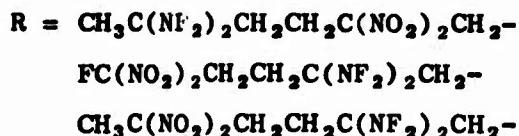
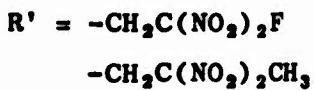
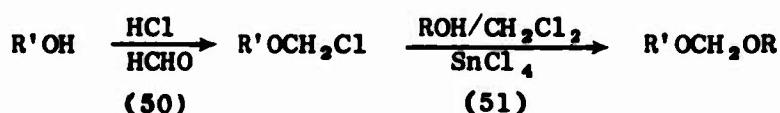
(C)



(C) Glycerol in dioxane was treated with potassium to give the insoluble monopotassium glyceroxide,^{10,11} Eq. (47). The resulting suspension was stirred with trinitroethane and a small amount of DMSO in an attempt to obtain α -(potassium dinitroethoxy)-glycerol,¹² Eq. (48). The orange solid that formed was immediately filtered, dissolved in water, and acidified, Eq. (49). Extraction of the aqueous phase with ether gave only a trace of yellow oil whose ir spectrum appeared to be crude α -dinitroethoxyglycerol, Eq. (49). Work on these reactions was not completed because of the change in the work statement, and because the initial results were not promising.

C. Nitrodifluoramino Formals (U)

(C) Research on the synthesis of the proposed formals as plasticizers started in November. The structures of these compounds are given in Table III. We had planned to prepare all of the compounds listed, but due to the difficulties encountered in preparing some of the compounds and the work on SYFO and DIAD, not all were synthesized. The proposed synthetic route for all of the compounds is shown in the following generalized reaction scheme, Eqs. (50) and (51).



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(C) The results of each synthesis are described in Table III along with the physical properties determined for those compounds prepared.

Table III

(C) NO₂-NF₂ FORMAL PLASTICIZERS (C)

Code Name	Structure - Properties	Remarks
YXOX	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_3$ $\text{C}_{10}\text{H}_{16}\text{N}_6\text{O}_{10}\text{F}_4 = 456.28 \rho = 1.46$ $\text{vp} = 0.1 \mu (25^\circ), 0.97 \mu (35^\circ)$ $\text{Dta} = 242^\circ \text{ exo } n_D (25^\circ) 1.4522$	Previously prepared on Contract NO0017-69-C-4412, 31% yield not optimized.
YXOF	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$ $\text{C}_9\text{H}_{13}\text{N}_6\text{O}_{10}\text{F}_5 = 460.24, \rho = 1.53, \text{Dta} = 208^\circ \text{ exo}$ $\text{vp} < 0.01 \mu 21^\circ \text{ C } \Delta H \text{ vap} = 21 \text{ kcal}$	28% yield not optimized.
FYOX	$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_3$ $\text{C}_9\text{H}_{13}\text{N}_6\text{O}_{10}\text{F}_5 = 460.24$	Synthesis attempted. Desired product not obtained.
FYOF	$\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$	Product contains 50% of $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{O}]_2\text{CH}_2$ as inseparable impurity.
XYOF	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$ $\text{C}_9\text{H}_{13}\text{N}_6\text{O}_{10}\text{F}_5 = 460.24$	Synthesis attempted. Desired product not obtained.
XYOX	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_3$ $\text{C}_{10}\text{H}_{16}\text{N}_6\text{O}_{10}\text{F}_4 = 456.28$	Synthesis not completed.

1. 2,2-Bis(difluoramino)-5,5,11,11-tetranitro-7,9-dioxadodecane

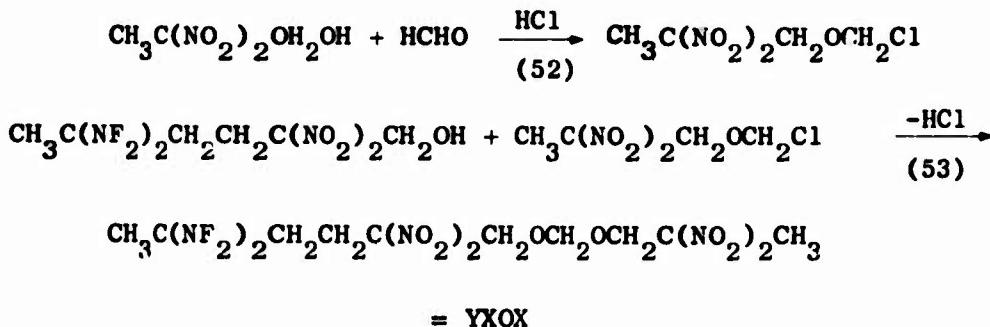
(YXOX) (C)

(C) Compound YXOX was prepared on a previous contract (Contract NO0017-69-C-4412) using the general method already described. Specifically dinitropropanol was treated with formaldehyde and HCl to give dinitropropyl chloromethyl ether, Eq. (52), which was then treated with bis(difluoramino)dinitrohexanol and stannic chloride in methylene chloride solution to give YXOX, Eq. (53). The vapor pressure, heat

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(C) stability, and compatibility of YXOX with P-GFDNE was very favorable, although its density of 1.46 was lower than desired. Since the objectives were the synthesis of low-volatility, energetic plasticizers with densities greater than 1.56 to 1.59, synthesis of the other compounds in Table III was undertaken.



2. 2,2-Bis(difluoramino)-11-fluoro-5,5,11,11-tetranitro-7,9-dioxaundecane (YXOF) (C)

(C) Compound YXOF was prepared by the method used for YXOX, except that fluorodinitroethanol was used in lieu of dinitropropanol. See Appendix A. Because of the presence of the fluorodinitromethyl group, YXOF was more dense (1.53) than YXOX (1.46). In all other respects, the two compounds had nearly the same physical properties. Its dta was run, and it was found to exotherm at 208°C. The vapor pressure of YXOF was found to be less than 0.01μ at 21°C.

3. 4,4-Bis(difluoramino)-1-fluoro-1,1,10,10-tetranitro-6,8-dioxaundecane (FYOX) (C)

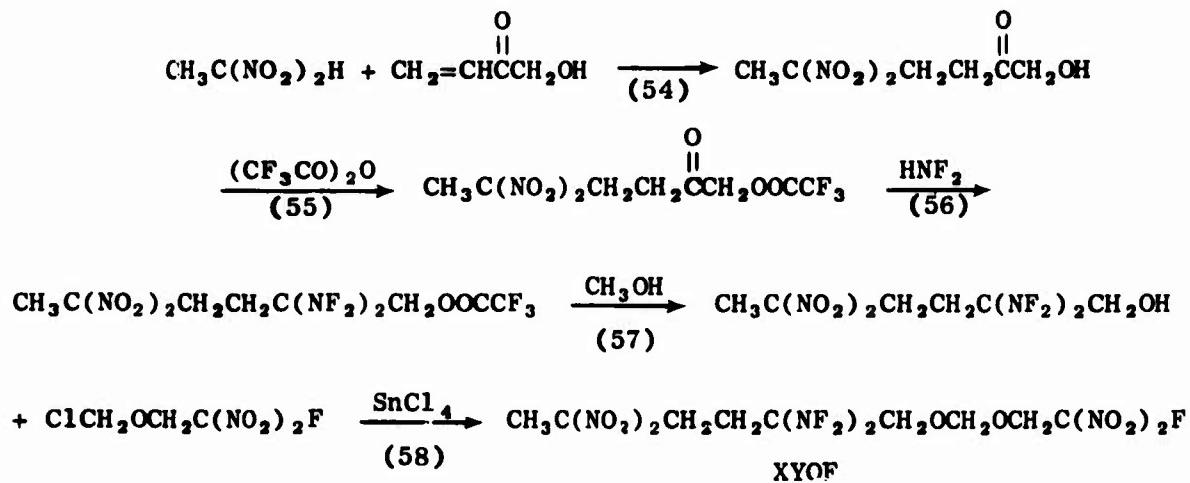
(C) Synthesis of FYOX, attempted only once, gave an unidentifiable liquid product whose nmr spectrum was consistent with the desired product in all but one respect; no signal for the $-\text{C}(\text{NF}_2)_2\text{CH}_2\text{O}$ protons was observed. Since FYOX was not expected to be as dense as the related derivative FYOF, work on FYOX was postponed in preference to the preparation of FYOF.

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(C) 4. 5,5-Bis(difluoramino)-11-fluoro-2,2,11,11-tetranitro-7,9-dioxaundecane (XYOF) (C)

(C) For the synthesis of XYOF, fluorodinitroethyl chloromethyl ether and bis(difluoramino)dinitrohexanol were treated with stannic chloride in methylene chloride, Eq. (58). Bis(difluoramino)dinitrohexanol was prepared by the reactions shown in Eqs. (54-57). (See Appendixes B, C, and D.)



The product was worked up in the manner described for the other goal compound. The nmr of the product was not consistent with the XYOF structure. As observed in the attempted preparation of FYOX, no signal for the $\text{C}(\text{NF}_2)_2\text{CH}_2\text{O}$ protons was present. We made no further attempts to prepare this compound, since other proposed formals could be prepared readily and appeared to be more promising candidate plasticizers.

5. 5,5-Bis(difluoramino)-2,2,11,11-tetranitro-7,9-dioxadodecane (XYOX) (C)

(C) No attempts were actually made to prepare XYOX because of the difficulties encountered in the synthesis of XYOF, and because of the success of other candidate plasticizers.

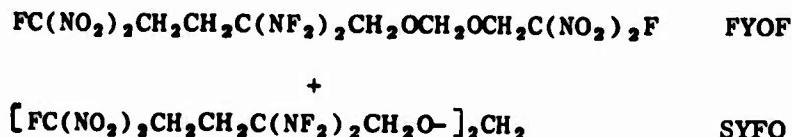
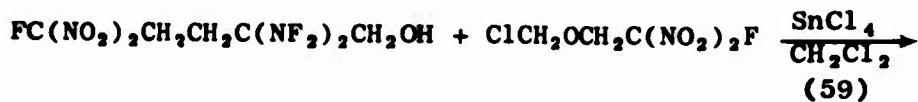
6. 4,4-Bis(difluoramino)-1,10-difluoro-1,1,10,10-tetranitro-6,8-dioxadecane (FYOF) (C)

(C) For the synthesis of FYOF, fluorodinitroethyl chloromethyl ether and bis(difluoramino)fluorodinitropentanol were treated with stannic

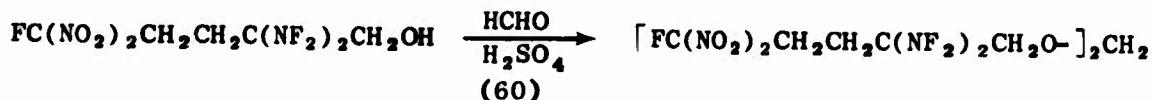
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(C) chloride, Eq. (59), and the product was worked up in the manner described for YXOF (Appendix A). The product was identified by nmr as a 1:1 mixture of the desired FYOF and SYFO, bis[fluorodinitro-bis(difluoramino)pentyl] formal.



Attempts to separate the two compounds by distillation and column chromatography were not successful. Therefore, to prove conclusively the structure of the symmetrical formal, it was synthesized by a known method,¹³ Eq. (60), by reaction of the domino alcohol with formaldehyde in 96% sulfuric acid (see Appendix J).



The synthesis and properties of the symmetrical formal will be discussed in detail in the next section. Because of the expected high density of FYOF, several additional attempts were made to prepare it free of the symmetrical formal. The results of this research are shown in Table IV.

(C) The results fall into two distinct categories. When pyridine or zinc chloride was used as catalyst, the starting alcohol, fluorodinitro-bis(difluoramino)pentanol, was recovered quantitatively. With other Lewis acid catalysts, the starting alcohol rapidly disappeared. No higher boiling products formed, and no alcohol was recovered after work-up. Therefore, we reasoned that the other catalysts were promoting decomposition of the alcohol via the cyclic mechanism shown below in Eq. (61).

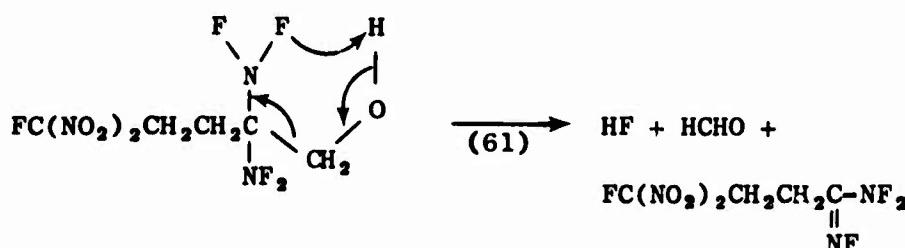
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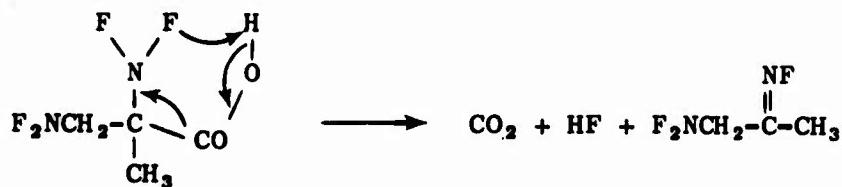
(C)

Table IV
(C) ATTEMPTED SYNTHESIS OF FYOF (U)

Catalyst	Time, hr	Temp, °C	CH ₂ Cl ₂ , ml	Remarks
Pyridine (1 equiv)	24	50	--	No reaction
AlCl ₃	1/4	25	10	Decomposition
BF ₃ · Et ₂ O	1/2	25	10	Decomposition
SbCl ₃	1	25	10	Decomposition
ZnCl ₂	72	40	10	No reaction



This mechanism has been proposed previously¹⁴ to explain the decomposition of 2-methyl-2,3-bis(difluoramino)propionic acid to give carbon dioxide and hydrofluoric acid, Eq. (62).



(C) Therefore, in our attempts to prepare FYOF using stannic chloride as a catalyst, it appears very likely that decomposition provides a source of formaldehyde, Eq. (61), for the formation of the symmetrical formal, see Eq. (59). Thus stannic chloride catalyzed both FYOF formation and alcohol decomposition, whereas the other Lewis acids catalyzed the alcohol decomposition exclusively.

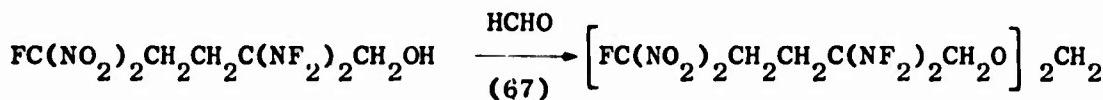
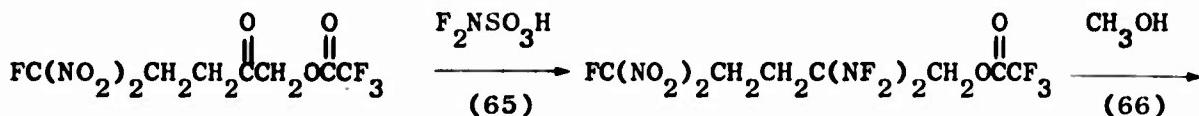
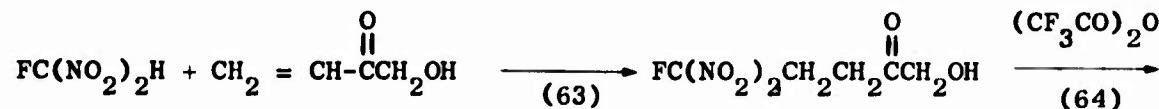
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(C) We felt that reaction (61) might be prevented if the stannic chloride were added in the form of a complex with fluorodinitroethyl chloromethyl ether. However, a substantial amount of SYFO was observed by glpc when this was done. Since FYOF and SYFO cannot be separated conveniently, additional work on FYOF was discontinued.

7. Bis[5-fluoro-5-dinitro-2,2-bis(difluoramino)pentyl]formal (SYFO) (C)

(C) The synthesis of the symmetrical formal (SYFO) was mentioned earlier in this report. It was initially prepared in 25% yield as a clear, colorless liquid with a density of 1.63. The dta had an exotherm at 210°C, and its vapor pressure was found to be 0.014μ at 21°C. Since this compound appeared to be a better candidate plasticizer than any of the six formals proposed, a 5-g sample was prepared and submitted to AFRPL for testing; initial tests appeared promising. Therefore, we began an investigation to improve the synthetic procedure as much as possible. The entire synthetic route is shown below in Eqs. (63-67).



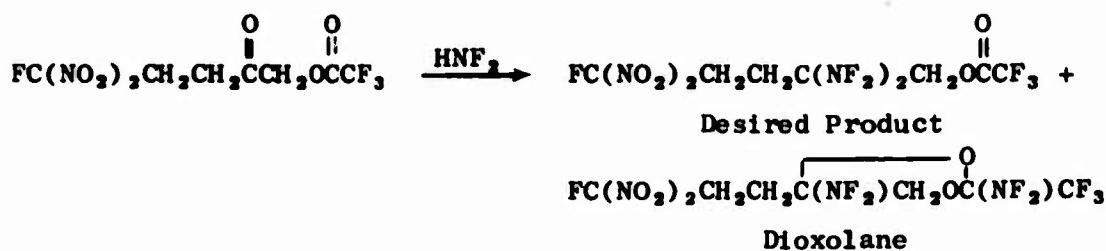
SYFO

(C) The addition of fluorodinitromethane to hydroxymethyl vinyl ketone and the esterification with trifluoroacetic anhydride are well known reactions and proceed in good yield without difficulty, Eqs. (63) and (64). However, during the difluoroamination, Eq. (65), we found

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(C) that substantial amounts of 2-difluoramino-2-trifluoromethyl-4-difluoramino-4-(3-fluoro-3,3-dinitropropyl)-1,3-dioxolane were formed in addition to the desired product, Eq. (68).



We also found that the ratio of dioxolane to desired product depended on the conditions under which the difluoramination was run. To find the best conditions to minimize formation of the dioxolane, a series of reactions was run in which the reaction time and temperature were varied. We found that other reaction variables did not particularly influence the product yield. The results of this research are shown in Table V.

Table V

DIFLUOROAMINATION OF 5-FLUORO-5,5-DINITRO-2-OXOPENTYL TRIFLUOROACETATE^a (C)

Run	Starting Material, mol	DFSA, mol ^b	Addition Temp, °C	Reaction Temp, °C	Reaction Time, hr	Desired Prod. %	Dioxolane %
1	0.049	0.18	0-5	0-5	1/2	25	75
2	0.049	0.18	0-5	0-5	1/2	25	75
3	0.023	0.09	0-5	0-5	1/2	30	70
4	0.023	0.12	0-5	0-5	3	37	63
5	0.012	0.15	0-5	0-5	2	25	75
6	0.033	0.19	0-5	25-30	2	77	23
7	0.033	0.10	0-5	25-30	2	75	25
8	0.033	0.10	0-5	25-30	2	54	46
9	0.048	0.20	0-5	25-30	2	76	20
10	0.049	0.18	8-10	25-30	1/2	58	42
11	0.049	0.18	8-10	25-30	1	71	24
12	0.049	0.18	0-5	25-30	1	64	36
13	0.049	0.18	0-5	25-30	1	64	36

^a All runs carried out in two-phase system of 100% sulfuric acid and methylene chloride.

^b Difluorosulfamic acid.

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(C) The best results were obtained from Runs 6, 7, 9, 11, 12, and 13. The conditions for these difluoroaminations are very much like those used in the batch process developed by Rohm and Haas for the difluoroamination of trifluoroacetoxy acetone.¹⁵ One of the critical factors in the reaction appeared to be the reaction temperature. Although the temperature at the time of addition of starting material to difluorosulfamic acid did not seem to have a significant effect, a reaction temperature of 25-30°C was required to obtain consistently high yields of the desired product.

(C) After further investigation we found that if the reaction was carried out in the presence of 1.4 equivalents of SO_3 , then dioxolane formation was eliminated completely, and the desired product was obtained in 76% yield and better than 95% purity.

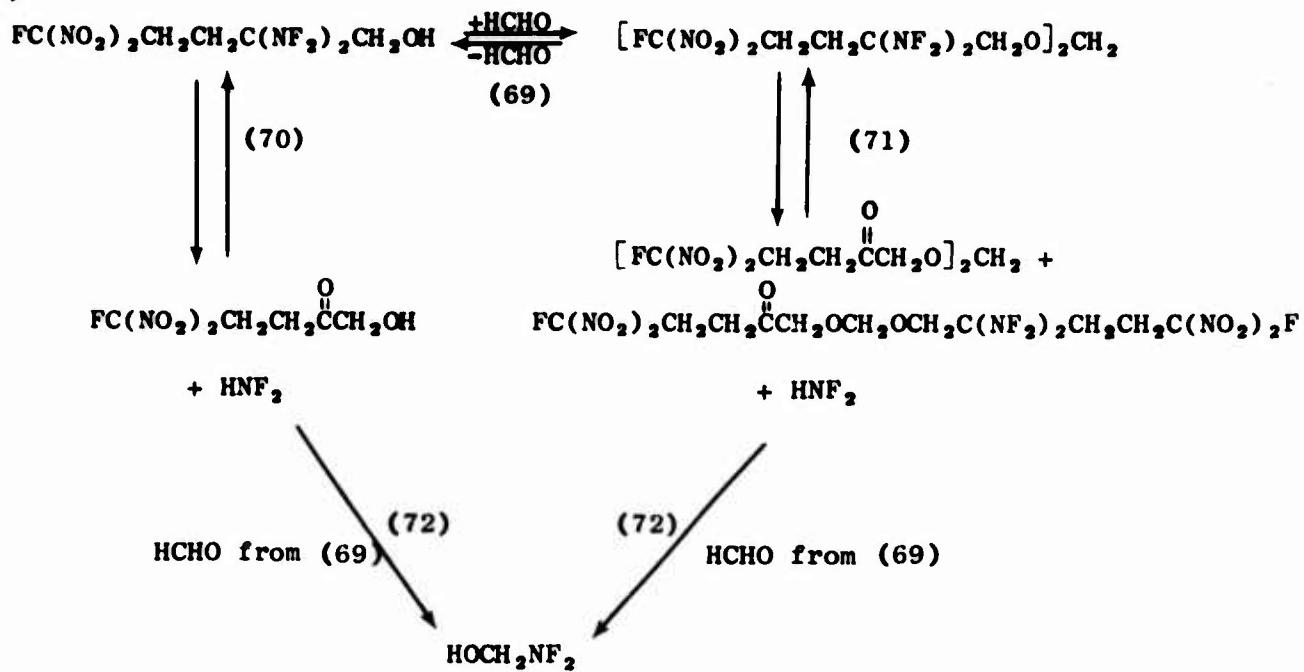
(C) The transesterification of 5-fluoro-5,5-dinitro-2,2-bis(difluoramino)pentyl trifluoroacetate in methanol, Eq. (66), proceeds readily and in 100% yield.

(C) The final step, Eq. (67), to give SYFO is far more complicated than any of the others. It involves a number of complex equilibria as well as an undesired side reaction. We found that the ratio of reactants and the amount of sulfuric acid catalyst critically affected both the equilibrium of the desired reaction and the side reaction. The side reaction is one in which difluoramino compounds in the presence of sulfuric acid, Eqs. (70) and (71), undergo the loss of HNF_2 . The rate of this reaction is dependent on the amount of formaldehyde present. To force the equilibrium of Eq. (69) toward product formation, an excess of formaldehyde must be used,¹³ but if too large an excess is used, it facilitates the loss of HNF_2 from the alcohol and formal, Eqs. (70) and (71). Although the loss of HNF_2 from the alcohol and formal is a reversible reaction, the formaldehyde drives the reaction to completion by reacting with the HNF_2 to give difluoraminomethanol, Eq. (72).

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(C)



(C) After a series of small-scale reactions were run under a variety of conditions, we found that a mole ratio of 1.5:2, formaldehyde:alcohol, gave the highest yield of formal with minimum loss of the alcohol in the side reaction, see Table VI.

(C) When an excessive amount of sulfuric acid was added to the reaction mixture as in Run 2, the equilibrium was reversed, and the formal returned to the alcohol even though excess formaldehyde had also been added. When a large excess of formaldehyde was added to a reaction mixture as in Run 3, loss of HNF_2 from the starting alcohol and the formal occurred. The optimum ratio of alcohol to formaldehyde to sulfuric acid was obtained in Run 9.

(C) The procedures discussed above are adequate for the preparation of SYFO on a small scale. However, to produce larger quantities, we began investigations to modify some of the procedures in order to reduce the hazard of large scale work, and also to determine whether or not the experimental procedures are adaptable to large scale preparation. This work is discussed in the next section.

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Table VI

(C) PREPARATION OF SYMMETRICAL FORMAL (U)

Run	Starting Material, mmol	90% H ₂ SO ₄ , ml	HCHO, mmol	Time, hr	% Product ^a
1	2	0.2	4	3/4	< 5
2	2	0.2	4	18	< 5 ^b
3	57	6.0	290	18	< 5 ^c
4	3.3	0.15	2.2	1	25
5	3.3	0.56	3.7	1	< 5
6	5.7	0.28	4.3	1	15 ^d
7	6.3	0.20	4.3	1	15 ^d
8	.7	0.28	4.3	1	15 ^d
9	44	2.16	33	1	39 ^e

^a Based on glc, taken relative to amount of starting material remaining.

^b Initially gave 65% but decreased when a solution of 0.1 g of formaldehyde in 0.2 ml 90% sulfuric acid was added.

^c Initially gave 14% but decreased when gaseous formaldehyde was bubbled into the mixture.

^d Contained mostly dioxymethylene product because paraformaldehyde was not completely depolymerized.

^e Actual yield of recovered product after workup.

a. Investigation of Scale-up Procedures for SYFO (U)

(C) Since tests by AFRPL indicated that SYFO was a very promising candidate plasticizer, we began an investigation of methods of improving the synthetic procedure used for its preparation. The results discussed below are tentative and indicative only of what may be expected in the preparation of a pound of SYFO. For the preparation of several pounds for motor firings, the study of each step must be completed.

(C) The procedure which we have been using for the preparation of fluorodinitromethane (FDM), Appendix E, is quite hazardous because it involves isolation of potassium fluorodinitromethide. This hazard limits

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(C) the scale on which the reaction can be run. To facilitate the preparation of large quantities of FDM, we began investigation of procedures which would eliminate the necessity of isolating the potassium salt.

(C) Following a procedure developed at NOL, we prepared the sodium salt of FDM from fluorotrinitromethane (FTM) in methanol/water and acidified the salt in situ. This solution was added to hydroxymethyl vinyl ketone in the manner described previously. See Appendix F. The yield was moderate, but extraction of 5-fluoro-5,5-dinitro-2-oxopentanol was made difficult by the presence of the methanol used in the preparation of FDM. A duplicate reaction was run using a small amount of Triton X-100 surfactant instead of methanol but again the yield was poor. Because the fluorodinitromethide anion was not very stable in aqueous solution, the low yield of ketoalcohol was probably due to prior decomposition of FDM.

(C) Fluorodinitroethanol (FDNE) has been prepared in excellent yield by reducing FTM in the presence of formaldehyde. The addition of the fluorodinitromethide anion to formaldehyde occurs rapidly, and the anion has little opportunity to decompose. We ran a similar reaction by treating FDM with sodium hydroxide/hydrogen peroxide in the presence of hydroxymethyl vinyl ketone. The desired product was recovered in 20% overall yield. The overall yield from the procedure involving isolation of potassium fluorodinitromethide after deformylation of FDNE was 39%. The new method represents a substantial decrease in yield, however the reaction can be run on a much larger scale and more quickly. In addition, the difference in the cost of starting materials (FTM compared to FDNE) makes the new method quite attractive, especially since a substantial improvement in yield may be possible with optimization.

(C) For the purpose of reducing the cost and time required for the production of SYFO, these first two steps described above have the greatest potential for improvement.

(C) Preparation of the trifluoroacetate, Eq. (64), is a straightforward esterification. We have experienced some variations in the yield on large scale runs, which may be due to lack of purity of the starting

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(C) alcohol (which is not distilled) or to the length of time which the trifluoroacetate is heated during distillation. The distillation requires both low pressure and high temperature, and decomposition products have been observed in the pot residues after distillation. The reaction can be carried out on a large scale, but it may be necessary to distill the product in batches or to forego the distillation entirely depending upon whether or not impurities affect the subsequent difluoroamination reaction, see Appendix G.

(C) The difluoroamination of 5-fluoro-5,5-dinitro-2-oxopentyl trifluoroacetate, Eq. (65), has been by far the most hazardous step in the synthesis of SYFO, see Appendix H. Our usual method has been to isolate pure difluoramine to determine the amount available for reaction. We have now modified a procedure developed at Rohm and Haas,¹⁵ and isolation and condensation of difluoramine is no longer necessary. The procedure consists of bubbling the difluoramine directly into a cooled mixture of 30% fuming sulfuric acid and methylene chloride. The amount of difluorosulfamic acid (DFSA) available for reaction is then determined by iodometric titration. Using this method, it is never necessary for difluoramine to undergo a change of state, thus reducing the hazards considerably. Although large scale reactions have not yet been run, we do not anticipate any difficulty.

(C) Transesterification of the difluoroaminated material to give 5-fluoro-5,5-dinitro-2,2-bis(difluoramino)pentanol, Eq. (66), is rapid and gives a 100% yield of product, see Appendix I.

(C) As discussed previously, preparation of the formal, Eq. (76), involves a number of complex equilibria. We investigated several different procedures to improve the yield of the formal and to facilitate the purification procedure. A preliminary investigation of the preparation of formals in methylene chloride disclosed that FEFO could be prepared from FDNE in good yield. A mixture of fluorodinitroethanol, trioxane, and a catalytic amount of sulfuric acid in methylene chloride was refluxed under an inverse Dean-Stark trap. The formation of FEFO was observed by glc in a very short time. When this reaction was repeated

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(C) with fluorodinitrobis(difluoramino)pentanol, no formal was observed, and the alcohol disappeared within a few days. The sulfuric acid apparently catalyzed only decomposition of the alcohol. Since this was not successful, we conducted our subsequent investigations of the reaction in sulfuric acid solvent.

(C) To optimize the ratio of alcohol to formaldehyde, three small scale reactions were run for 5 hr in 95% sulfuric acid using alcohol: formaldehyde ratios of 2:1.0, 2:1.5, and 2:3.0. After work-up, the highest yield was obtained with a ratio of 2:1.5. Two additional reactions were run to determine (1) if the reaction time could be shortened, and (2) if the yield could be improved by using 100% sulfuric acid containing a trace of SO_3 . Both reactions were run for 2 hr using the optimum ratio of alcohol to formaldehyde. The mixture containing SO_3 showed a small increase in yield over the one containing 97% sulfuric acid. Therefore, all the remaining reactions were run using a trace of SO_3 .

(C) Yields of the small scale formal reactions were 60-65%. On a 10-g run, the yield was also 65% but decreased to 61% for 20 g, and 47% for a 40-g run. This decrease in yield with increase in scale may be due to the limited reaction time or the stirring efficiency because the reaction mixture contains two phases. As the reaction size increased, it became more difficult to maintain a homogenized mixture.

(C) An improved purification procedure for SYFO was used on each of the large scale runs discussed above. The crude reaction product was dissolved in 50:50 chloroform:hexane and passed through an aluminum oxide column. For the 40-g run, the column size was 4×50 cm, and 50-ml fractions were collected. The first fraction, which left a residue on evaporation (usually 1-2 g), contained no SYFO and was discarded. The next eight fractions contained SYFO and low boiling impurities. These were combined and placed under a vacuum of $< 5 \mu$ at 50°C for 24 hr to remove low boiling impurities. After this treatment the residual SYFO was clear and colorless and + 98% pure, see Appendix J. The physical properties of SYFO are listed in Appendix K.

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(C) The procedures discussed above are a considerable improvement over those originally used to prepare SYFO, but they should not be considered optimum.

b. Thermal Stability and Plasticization Study of SYFO (U)

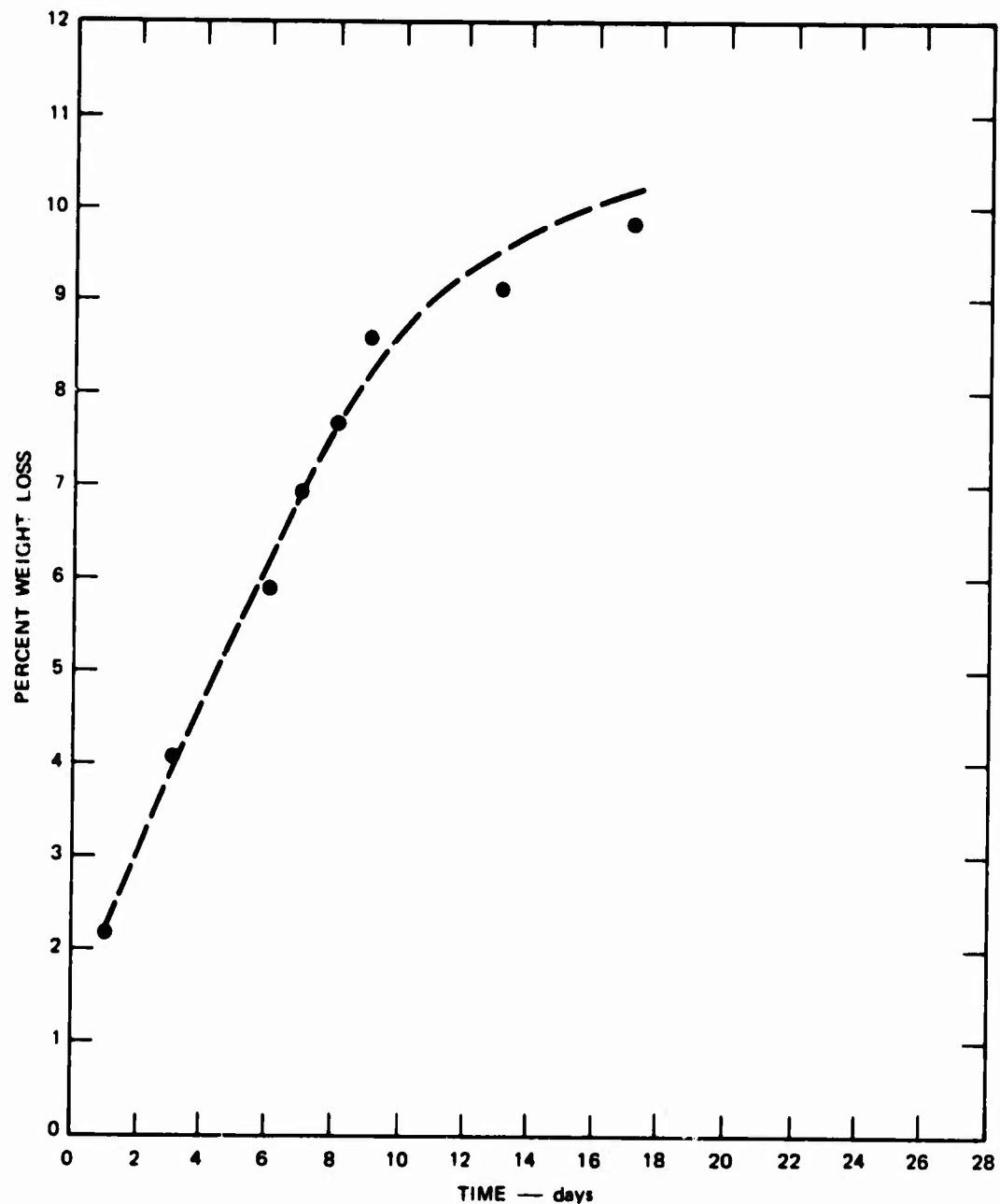
(C) A 0.16-g sample of SYFO (+99% pure) was placed in a flask open to the atmosphere through a very fine capillary and was stored in an oven at 100°C. The sample was weighed periodically and samples were removed for ir and glc analyses. At the end of eight days, there was no detectable change in the appearance of the sample nor in the ir or glc. The percent weight loss versus time is shown in Figure 1. On the 24th day, the ir showed a weak carbonyl absorption, and in the glc a new lower boiling component appeared. The sample was +85% pure at that time.

(C) The Air Force expressed an interest in the ability of SYFO to plasticize nitrocellulose. Therefore, we conducted a series of experiments with SYFO and also with FEFO and difluoro-FEFO for comparison purposes. Nitrocellulose films containing the following ingredients were prepared: (1) 50 mg NC, 150 mg TEGDN (reference), (2) 50 mg NC, 150 mg SYFO, (3) 50 mg NC, 50 mg TEGDN, 100 mg SYFO, (4) 50 mg NC, 150 mg FEFO, (5) 50 mg NC, 50 mg TEGDN, 100 mg FEFO, (6) 50 mg NC, 150 mg difluoro-FEFO, (7) 50 mg NC, 50 mg TEGDN, 100 mg difluoro-FEFO. Each of the components was dissolved in ethyl acetate, combined, and then poured into a watch glass. When the ethyl acetate had evaporated, the films were cured at 60°C for 6 hr.

(C) All of the films were clear and colorless. The films containing only the test compound with nitrocellulose were moderately pliable but broke more readily than the reference. Films containing TEGDN were nearly as pliable as the reference. Differences between the films cast with SYFO, FEFO and difluoro-FEFO were extremely small, and all three can be considered very good plasticizers for nitrocellulose.

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FIGURE 1 PERCENT WEIGHT LOSS OF SYFO VERSUS TIME AT 100°C (U)

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(C) c. Sensitivity of SYFO (U)

(C) Impact Sensitivity. Impact tests were run on a Technoproduts drop-weight tester using nitroglycerin and ethyl nitrate as reference samples. The results shown in Table VII indicate that SYFO is moderately sensitive to impact and should be handled with care.

Table VII

(U) IMPACT SENSITIVITY OF SYFO (U)

Ethyl nitrate (1 kg weight): 50% point = 1 kg-cm

Trial	0.5 cm	1 cm	2 cm
1	--	+	+
2		+	+
3	-		+
4	-		

Nitroglycerin (1 kg weight): 50% point = 1.5 kg-cm

Trial	1 cm	1.5 cm	2 cm
1	-	-	+
2	-	+	+
3	-	-	+
4	-	+	
5	-	-	
6		+	

SYFO (1 kg weight): 50% point = 4-5 kg-cm

Trial	2 cm	3 cm	4 cm	5 cm
1	-	-	+	+
2		+	+	-
3			-	-
4			-	+
5		+		
6		+		

(C) Electrostatic Sensitivity. The electrostatic test was run by charging a capacitor at a given voltage and discharging it through a 50-mg sample via a detonation cable. The gap at the end of the cable immersed in the sample was 0.1 mm. Lead azide was run as a reference and the results shown in Table VIII indicate that SYFO is not sensitive to electrostatic discharge.

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(C)

Table VIII

(U) ELECTROSTATIC SENSITIVITY OF SYFO (U)

Lead Azide

Run	Millijoules	Results
1	5	-
2	10	+
3	15	+

SYFO

1	40	-
2	80	-
3	80	-
4	80	-
5	80	-
6	80	-
7	83	+?
8	83	-
9	83	-
10	83	-

(C) Friction Sensitivity. A screw friction test apparatus was used to measure the friction sensitivity of SYFO. Lead azide was run as a reference, and SYFO was found to be insensitive to friction. The results are shown in Table IX.

Table IX

(U) FRICTION SENSITIVITY OF SYFO (U)

Lead Azide

Run	Mohs Hardness	Result
1 Bare Tool	-	-
2 Glass (100 mesh)	5.5	+

SYFO

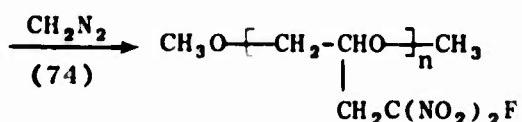
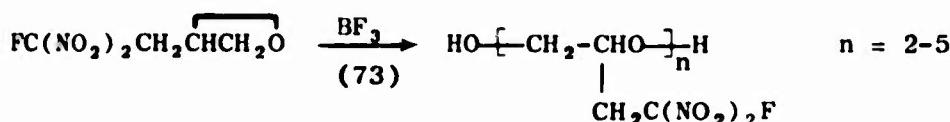
1	Bare Tool	-	-
2	Glass (100 mesh)	5.5	-
3	Silicon Carbide (100 mesh)	9	-
4	Silicon Carbide (100 mesh)	9	-
5	Silicon Carbide (100 mesh)	9	-
6	Silicon Carbide (100 mesh)	9	-

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(C) 8. 1,15-Difluoro-1,1,15,15-tetranitro-6,10-bis(2-fluoro-2,2-dinitroethyl)-3,5,8,11,13-pentaoxapentadecane (DIAD) (C)

(C) During the investigation of the synthesis of Compound IA, fluorodinitroepoxybutane was prepared. The Air Force expressed an interest in a low molecular weight polymer of fluorodinitroepoxybutane. We proposed to polymerize the compound and end-cap the polymer with diazomethane as shown in Eqs. (73) and (74).



Several polymerizations were carried out using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in ethylene dichloride with water present to terminate the chains. However, all reactions led either to very high molecular weight polymer or resulted in no polymerization, see Table X.

Table X

(C) POLYMERIZATION OF FLUORODINITROEPOXYBUTANE* (C)

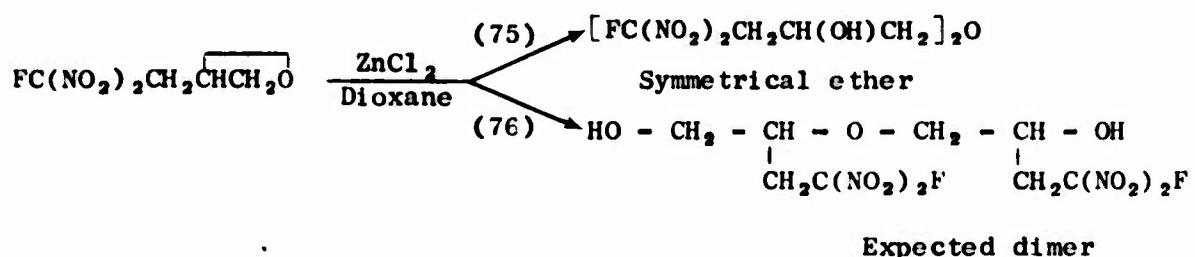
Run	Epoxide mmol	Water mmol	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ mmol	Conversion %	Remarks
1	20	4.8	0.4	< 1	No appreciable polymerization
2	5.6	0	0.26	80	Viscosity >> PGFDNE
3	5.6	1.3	0.11	60	Viscosity < PGFDNE
4	5.6	0.8	0.22	70	Viscosity = Run 3

* All runs carried out in 25 ml ethylene dichloride as solvent.

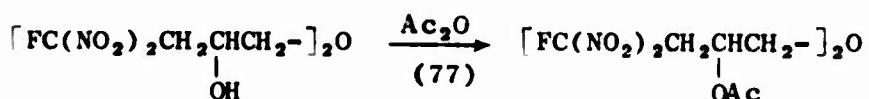
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(C) Three additional small scale polymerizations were carried out using different catalysts and solvent systems. Stannic chloride in benzene polymerized all of the monomer in less than 15 min at ambient temperature to give a very viscous oil. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in dioxane reacted equally fast and also gave a viscous oil. Zinc chloride in dioxane did not react after 4 hr at 25°C. After standing at 83°C for 3 days, all of the monomer had reacted to give a product which could be isolated by glc. The product was purified by liquid chromatography, and the nmr of the product indicated that it was the symmetrical ether, bis[4-fluoro-4,4-dinitro-2-hydroxybutyl]ether, Eq. (75), rather than the expected dimer, Eq. (76). See Appendix L.



(C) To confirm the structure of the symmetrical ether we prepared its diacetate, Eq. (77), and compared the nmr of both.

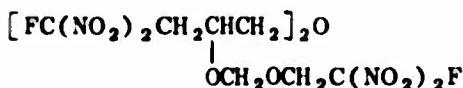
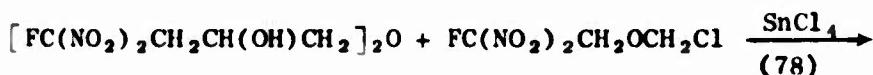


The $\overset{\text{OH}}{\text{CH}}$ - protons of the ether appeared as a multiplet at τ 5.73, whereas the $\overset{\text{OAc}}{\text{CH}}$ - protons of the diacetate showed the same multiplet shifted downfield to τ 4.60. Had the ether been the dimer shown in Eq. (76), only one-half of the $\overset{\text{OH}}{\text{CH}}$ - protons would have been shifted downfield by conversion to the acetate.

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(C) Attempts to end-cap the dimer with diazomethane were unsuccessful. Normally, only acidic alcohols will react with diazomethane without the presence of a Lewis acid catalyst.¹⁶ When a catalyst is used there is a competing reaction; the diazomethane tends to form polymethylene, and the ability of the alcohol to compete with this side reaction depends again on its acidity.¹⁷ Apparently the symmetrical ether is not sufficiently acidic to give significant amounts of the desired product.

(C) However, we found that the symmetrical ether could be end-capped by converting the alcohol groups to formals with fluorodinitroethyl chloromethyl ether, Eq. (78), to give DIAD, see Appendix M.



DIAD

(C) DIAD is a distillable colorless liquid with bp 115°C (< 5μ). The physical properties of DIAD are given in Appendix N. A thorough study of DIAD was not completed due to the effort expended on the investigation of SYFO.

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Appendix A (U)

YXOF, 2-FLUORO-2,2-DINITROETHYL 5,5-BIS(DIFLUORAMINO)-2,2-DINITROHEXYL FORMAL (C)

(C) To a mixture of 1.47 g (5.0 mmol) of 5,5-bis(difluoramino)-2,2-dinitrohexanol, 1.83 g (10 mmol) of fluorodinitroethyl chloromethyl ether, and 5 ml of methylene chloride at 25°C was added 3 drops of stannic chloride. The reaction mixture was stirred at 40°C for 48 hr. It was then cooled and diluted with 25 ml of methylene chloride, washed with 10 ml 5% sodium bicarbonate, dried over magnesium sulfate, filtered, and evaporated leaving 1.8 g yellow liquid.

(C) The liquid was dissolved in chloroform and passed through a silica gel column (1 x 50 cm). The first 15-ml fraction (collected from the first positive TMPDA test) contained 1.4 g. The unreacted fluorodinitroethyl chloromethyl ether was removed at 0.005 mm (40°C) leaving 0.6 g (28% yield) of the desired product. A small sample for analysis was distilled at 140°C (0.005 mm): ir (neat) 3.4 (w), 6.8 (m), CH; 6.1 - 6.3 (s), 7.5 (s), NO₂; 8.8 (m), 9.4 (s), 9.9 (m), 10.2 (m), 10.9 (m), 11.6 (m), 12.35 (m), unassigned. nmr (CDCl₃) τ 5.22 (s, OCH₂O), 5.43 (d, FC(NO₂)₂CH₂, J = 17 Hz), 5.53 (s, CNO₂CH₂O), 7.15 (m, CNO₂CH₂CH₂), 7.88 (t, CH₂CNF₂, J = 16 Hz), 8.34 (quin, CH₂CNF₂, J = 2 Hz). Anal Calcd. for C₉H₁₃N₆O₁₀F₅: C, 23.48; H, 2.83; N, 18.26. Found, C, 24.06; H, 2.77; N, 17.60.

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Appendix B (U)

5,5-DINITRO-2-OXOHEXYL TRIFLUOROACETATE (C)

(C) To a mixture of 12.0g (0.14 mol) of sodium carbonate and 115 ml of methylene chloride at 0°C was added dropwise 11.2g (0.053 mol) of trifluoroacetic anhydride. To this mixture was added a solution of 7.2 (0.035 mol) of 5,5-dinitro-2-oxohexanol* in 37 ml of methylene chloride dropwise at 0° - 5°C. The reaction mixture was stirred at 0°C for 1 hr and then refluxed for 1-1/2 hr. The mixture was cooled to 25°C, stirred for an additional hour and filtered. The filtrate was evaporated to give a dark oil which crystallized on cooling. The product was recrystallized from chloroform/hexane to give 5.1g (49%) of tan crystals: mp 63°-65°C, ir (melt) 3.3 (w), 6.85 (m), CH; 5.55 (s) CF₃CO; 5.7 (s), C=O; 6.3 (s), NO₂; 8.1 (s), 8.5 μ (s), COC.

* E. E. Hamel, Tetrahedron, 19, Suppl. 1, 85, (1963).

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Appendix C (U)

2,2-BIS(DIFLUORAMINO)-5,5-DINITROHEXYL TRIFLUOROACETATE (C)

(C) To a mixture of 0.18 mol of difluorosulfamic acid in 25 ml of 100% sulfuric acid and 25 ml of methylene chloride at 0°C was added dropwise a solution of 5.1 g (0.017 mol) of 5,5-dinitro-2-oxohexyltrifluoroacetate in 25 ml of methylene chloride. The reaction mixture was stirred for 3 hr at 25°C. The organic phase was separated, dried over magnesium sulfate, filtered, and evaporated leaving 5.0 g of colorless liquid.

(C) The liquid was dissolved in chloroform and passed through a silica gel column (1 x 25 cm). Fractions of 10 ml were collected from the first positive TMPDA test. The first two fractions contained 4.4 g (67%) of the desired product: ir (neat) 3.3 (w), 6.8 (m), CH; 5.5 (s), CF₃C=O; 6.4 (s), NO₂; 8.4 (s), 8.6 (s), COC; 10.0 (m), 10.9 μ (s), NF₂.

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Appendix D (U)

2,2-BIS(DIFLUORAMINO)-5,5-DINITROHEXANOL (C)

(C) A solution of 4.4 g (0.011 mol) of 2,2-bis(difluoramino)-5,5-dinitrohexyl trifluoroacetate and 50 ml methanol was refluxed for 1 hr. The methanol was removed on a rotary evaporator leaving 3.4 g (100%) of colorless liquid: ir (neat) 2.8 (m), OH; 3.4 (w), 6.8 (m), CH, 6.3 (s), NO₂; 10.0 (s), 10.9 μ (s), NF₂; nmr (CDCl₃) τ 5.85 (CNF₂CH₂O, s), 7.19 (OH, s), 7.19 (CNO₂CH₂, m), 7.76 (CNF₂CH₂C, t, J = 8 Hz), 7.85 (CH₃CNO₂, s).

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Appendix E

FLUORODINITROMETHANE (C)

(C) To a solution of 25.0 g (0.38 mol) of potassium hydroxide in 100 ml of methanol at 0 to -5°C was added a solution of 50 g (0.32 mol) of fluorodinitroethanol in 200 ml of methanol dropwise over 20 min. During the addition, 50 ml of methylene chloride was added to facilitate stirring. After the addition was complete, the reaction mixture was cooled to -35°C. During the remainder of this procedure the potassium salt was kept cold and wet. All of the materials and the apparatus were precooled to -78°C.

(C) The potassium salt was filtered and washed twice with 200-ml portions of methylene chloride. The filtrate was discarded, and 200 ml of 2N sulfuric acid was added to the salt. Acidification was carried out in the same funnel and, when the reaction was complete, it was filtered using the same funnel again. The filtrate was extracted 4 times with 75-ml portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate, filtered, and evaporated to give 20 g of fluorodinitromethane, 57% yield.

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Appendix F

5-FLUORO-5,5-DINITRO-2-OXOPENTANOL (C)

(C) Hydroxymethyl vinyl ketone was generated in situ according to the following procedure. A mixture of 135 g (1.57 mol) of 2-butyne-1,4-diol, 5.2 ml of 97% sulfuric acid, 8.0 g of mercuric sulfate, and 800 ml of water was stirred at 50°C for 1 hr. The mixture was then cooled to 25°C and filtered. To the filtrate was added a solution of 90 g (0.725 mol) of fluorodinitromethane in 600 ml of water at 25°C over 20 min. The reaction mixture was stirred under a nitrogen atmosphere for 18 hr. It was then saturated with sodium chloride and extracted 3 times with 200-ml portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate, filtered, and evaporated to give 117 g of product, 77% yield.

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Appendix G

5-FLUORO-5,5-DINITRO-2-OXOPENTYL TRIFLUOROACETATE (C)

(C) To a stirred suspension of 193 g (1.82 mol) of sodium carbonate in 1300 ml of methylene chloride at 0°C was added 179 g (0.85 mol) of trifluoroacetic anhydride dropwise over 30 min. To this mixture at 5°C was added a solution of 117 g (0.56 mol) of 5-fluoro-5,5-dinitro-2-oxopentanol in 400 ml of methylene chloride dropwise over 1 hr. The reaction mixture was stirred at 5°C for 1.5 hr, refluxed for 1.5 hr, and then stirred at 25°C for 1 hr. The mixture was then filtered and evaporated to give 120 g of crude product. This was distilled through a short column at 110-120°C (0.1 mm) to give 100 g of pure product, 58% yield.

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Appendix H

5-FLUORO-5,5-DINITRO-2,2-BIS(DIFLUORAMINO) PENTYL TRIFLUOROACETATE (C)

(C) Difluoramine was generated by adding 150 ml of a 3-molar difluorocurea solution to 60 ml of 4N sulfuric acid at 95-100°C over 20 min. The difluoramine was bubbled directly into a mixture of 88 g (0.33 mol of SO₃) of 30% fuming sulfuric acid and 30 ml of methylene chloride at 0-5°C. An aliquot of the DFSA solution was removed and found to contain 0.24 mol DFSA by iodometric titration.

(C) To the DFSA solution at 0-5°C was added dropwise over 30 min a solution of 15 g (0.049 mol) of 5-fluoro-5,5-dinitro-2-oxopentyl trifluoroacetate in 25 ml of methylene chloride. When the addition was complete, the reaction mixture was warmed to 25°C and stirred for 2 hr. The acid phase was then separated and extracted with 25 ml of methylene chloride. The methylene chloride solutions were combined, dried over magnesium sulfate, filtered, and evaporated leaving 14.6 g of product, 76% yield.

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Appendix I

5-FLUORO-5,5-DINITRO-2,2-BIS(DIFLUORAMINO)PENTANOL (C)

(C) A solution of 14.6 g (0.037 mol) of 5-fluoro-5,5-dinitro-2,2-bis(difluoramino)pentyl trifluoroacetate in 50 ml of methanol was refluxed for 10 min. The methanol was then removed in vacuo to give 11.0 g of product, 100% yield, >95% purity on the basis of glc analysis.

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Appendix J

BIS[5-FLUORO-5,5-DINITRO-2,2-BIS(DIFLUORAMINO)PENTYL]FORMAL (SYFO) (C)

(C) A mixture of 1.5 ml of 100% sulfuric acid containing a small amount of SO₃, and 0.68 g (0.025 mol of formaldehyde) of trioxane was stirred for 10 min. This was then cooled to 10°C and 9.8 g (0.033 mol) of 5-fluoro-5,5-dinitro-2,2-bis(difluoramino)pentanol was added dropwise over 15 min at 10-15°C. The reaction mixture was stirred vigorously for 2 hr at 25°C and then poured into a rapidly stirred mixture of 40 g of ice/water and 40 ml of methylene chloride. The organic phase was separated and the aqueous phase extracted twice more with 40 ml of methylene chloride. The methylene chloride solutions were combined, dried over magnesium sulfate, filtered, and evaporated leaving 8.7 g of crude product. This was dissolved in a 50:50 mixture of chloroform:hexane and passed through an aluminum oxide column. Fractions of 20 ml were collected. The product (6.8 g) came out in fractions 4-8. The fractions were combined and stirred vigorously at 50°C ($\text{d}\mu$) for 24 hr. The residue of 6.6 g was analyzed by glc and found to be >99% pure, 65% yield.

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Appendix K

PROPERTIES OF BIS[2,2-BIS(DIFLUORAMINO)-5-FLUORO 5,5-DINITROPENTYL] FORMAL (SYFO) (C)

Structure:	$[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{O}]_2\text{CH}_2$
Empirical formula:	$\text{C}_{11}\text{H}_{14}\text{F}_{10}\text{N}_8\text{O}_{10}$
Formula weight:	608.29
Appearance:	Colorless solid
Melting point:	29 °C
Vapor pressure:	0.047 μ (35.2°C), 0.014 μ (20.7°C)
Density:	1.64 (25°C)
ΔH_{vap} :	15.0 kcal/mol, 2.5 kcal/100g
ΔH_f^0 (g) estimated:	-253.26 kcal/mol, -41.63 kcal/100g
ΔH_f^0 (l) estimated:	-268.26 kcal/mol, -44.13 kcal/100g
DTA:	Exo 230°C (onset 200°C)
Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{F}_{10}\text{N}_8\text{O}_{10}$:	C, 21.72; H, 2.32; N, 18.42.
Found:	C, 22.01; H, 2.48; N, 17.64.

Infrared spectrum (neat): 3.3 (w), 3.4 (w), 6.85 (w), CH; 6.2 (s), 7.5 (m), NO₂; 8.7 (m), 9.3 (m), 10.0 (m), 10.9 μ (m), unassigned.
Nmr (CDCl₃): τ 5.25 (s, OCH₂O), 5.88 (s, CNF₂CH₂O), 6.87 (m, CNO₂CH₂), 7.62 (t, CNF₂CH₂C, J = 8 Hz); φ -26.6 (s, NF₂), +103 (t, FCNO₂, J = 18 Hz).

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Appendix L (U)

BIS[4-FLUORO-4,4-DINITRO-2-HYDROXYBUTYL] ETHER (C)

(C) A mixture of 1.7 g (9.45 mmol) of 4-fluoro-4,4-dinitroepoxybutane, 0.50 g (3.67 mmol) of zinc chloride, and 4.1 g of dioxane was stirred at 80°C for 4 days. The reaction mixture was cooled, diluted to 25 ml with methylene chloride, and filtered. The filtrate was washed with water, dried over magnesium sulfate, filtered, and evaporated to give 1.2 g of yellow liquid.

(C) The product was dissolved in a 25:75 mixture of chloroform:hexane and passed through a cellulose column (1 x 25 cm). Fractions of 10 ml each were collected. The third, fourth, and fifth fractions contained 0.7 g (37%) of product: ir (neat) 2.8 (m), OH; 3.4 (w), 6.9 (m), CH; 6.2 (s), 7.5 (m), NO₂; 8.9 (m), 9.2 μ (m), unassigned; nmr (acetone-d₆) τ 4.99 (OH, d, J = 5 Hz), 5.73 (CH, m), 6.37 (CH₂O, d, J = 5 Hz), 6.71 (CH₂CNO₂, m). To confirm the structure, the diacetate was prepared by the following procedure.

(C) A solution of 0.30 g of 4-fluoro-4,4-dinitro-2-hydroxybutyl ether in 10 ml of acetic anhydride was stirred at 80°C for 45 min. The reaction mixture was cooled to 10°C, poured into 30 ml of water, and stirred vigorously for 1 hr. The mixture was extracted 3 times with 10-ml portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate, filtered, and evaporated leaving 0.3 g of pale yellow liquid. Nmr (acetone-d₆) τ 4.60 (CH, m), 6.17 (CH₂O, d, J = 5 Hz), 6.44 (CH₂NO₂, m), 8.04 (CH₃, s).

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Appendix M (U)

DIAD (U)

(C) Ten drops of stannic chloride was added to a mixture of 2.27 g (0.006 mol) of bis[4-fluoro-4,4-dinitro-2-hydroxybutyl]ether, 4.36 g (0.024 mol) of fluorodinitroethyl chloromethyl ether, and 20 ml of methylene chloride at 25°C. The reaction mixture was refluxed for 72 hr and then diluted with 30 ml of methylene chloride. The solution was washed twice with 10 ml portions of 5% sodium bicarbonate. The methylene chloride solution was then dried over magnesium sulfate, filtered, and evaporated leaving 5.0 g of pale yellow liquid. This was placed under a vacuum of less than 5 μ at 70°C for 4 hours to remove the excess fluorodinitroethyl chloromethyl ether. A sample of the residue was distilled through a short path at 115°C (< 5 μ) to give a > 99% pure sample for analysis.

Ir (neat) 3.3 (w), 3.4 (w), 6.85 (w), CH; 6.2 (s), 7.55 (s), NO₂; 9.8 (m), COC; 11.65 (m), 12.4 μ (m), unassigned; nmr (acetone-d₆) τ 5.03 (d, CNO₂CH₂O, J = 17 Hz), 5.08 (s, OCH₂O), 5.54 (m, CH), 6.09 and 6.10, (d, CH₂O, J = 5 Hz, dl and meso), 6.45 (m, CNO₂CH₂C), ω 102 (broad singlet, FCNO₂CC), 108 (broad singlet, FCNO₂CO. Anal. Calcd for C₁₄H₁₈N₈O₂₁F₄: C, 23.67; H, 2.55; N, 15.77. Found: C, 22.08; H, 2.41; N, 14.28. The elemental analysis will be repeated when more material is available.

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Appendix N (U)

PROPERTIES OF 1,15-DIFLUORO-1,1,15,15-TETRANITRO-6,10-BIS-(2-FLUORO-2,2-DINITROETHYL)-3,5,8,11,13-PENTAOXAPENTADECANE (DIAD) (C)

Structure:	$\left[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{OCHCH}_2 \right]_2\text{O}$ $\text{CH}_2\text{C}(\text{NO}_2)_2\text{F}$
Empirical formal:	$\text{C}_{14}\text{H}_{18}\text{N}_8\text{O}_{21}\text{F}_4$
Formula weight:	710.35
Appearance:	Clear, colorless, mobile liquid
Boiling point:	140° (5μ)
Density:	1.53 (25°C)
ΔH_{vap} :	20.0 kcal/mol (estimated)
ΔH_f° (g) estimated:	-427.11 kcal/mol, -60.13 kcal/100g
H_f (l) estimated:	-447.11 kcal/mol, -62.94 kcal/100g
DTA:	Exo 240°C (onset 190°C)
Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{N}_8\text{O}_{21}\text{F}_4$:	C, 23.67; H, 2.55; N, 15.77
Found:	C, 22.08; H, 2.41; N, 14.28

Infrared spectrum (neat); 3.3 (w), 3.4 (w), 6.85 (w), CH; 6.2 (s), 7.55 (s), NO_2 ; 9.8 (m), COC; 11.65 (m), 12.4μ (m), unassigned; nmr (acetone -d₆) τ5.03 (d, $\text{CNO}_2\text{CH}_2\text{O}$, J = 17 Hz), 5.97 (s, OCH_2O), 5.54 (m, CH), 6.09 and 6.10 (d, CH_2O , J = 5 Hz, dl and meso), 6.45 (m, $\text{CNO}_2\text{CH}_2\text{C}$), φ102 (broad FCNO₂CC), 108 (broad, FCNO₂CO).

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13. ABSTRACT The primary objective of this research program was the synthesis of thermally stable, high density, and high energy plasticizers for new high energy polyether binders of interest to the Air Force. Initially the synthesis of three specific nitro-difluoramino-ether plasticizers was studied, but difficulties in synthesis and poor yields made their preparation impractical. The research effort was then redirected toward the synthesis of a series of nitrodifluoramino-formal plasticizers which resulted in the synthesis of SYFO, bis[5-fluoro-5,5-dinitro-2,2-bis(difluoramino)pentyl]formal. In overall properties, SYFO has outperformed all other energetic plasticizers known. Results of tests to date show that SYFO has the required high energy and density, low volatility, and thermal and chemical stability. In addition, SYFO imparts excellent properties to propellants formulated with it, and results in thermally stable propellants which heretofore have not been possible. A summary of work performed on this contract follows in order of performance. (C)

TDFH, 1,7-difluoro-1,1,7,7-tetrานитро-4,4-bis(difluoramino)heptane, which was discovered on a previous Navy contract, was prepared in larger quantities and submitted to AFRPL for evaluation as a plasticizer for P-GFDNE, and for PCDE. TDFH was found to be a very good plasticizer for these binders during formulation, but after curing, the propellant became brittle. This was probably due to a low degree of association between TDFH and other ingredients or the fact that a lower eutectic point was not achieved at the concentration of TDFH used. (C)

Nitrodifluoramino ethers were studied in order to obtain plasticizers similar in structure to TDFH but lower melting. Compounds studied included Goal Compounds I, IA, and II:

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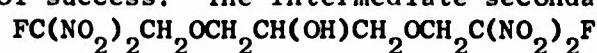
14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High energy plasticizers High density plasticizers Thermally stable plasticizers Fluoronitro-ether plasticizers Difluoramino-fluoronitro-ether plasticizers Difluoramino-fluoronitro-alkane plasticizers Thermal stability tests Sensitivity tests						

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Compound I, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$. Two synthetic approaches to Compound I were investigated. The first involved the addition of fluorodinitroethanol to epoxybutene. The reaction was carried out in base, but the epoxide opening was catalyzed by the acidic alcohol, fluorodinitroethanol, rather than the base. The resulting product was the undesired isomer. A second approach to the synthesis utilized a metathetical reaction between fluorodinitromethane and iodobutene. The desired product was obtained, but the yield was never greater than 5%. (C)

Compound IA, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$. The synthesis of Compound IA was partially completed. Fluorodinitroepoxybutane was prepared by a metathetical reaction between fluorodinitromethane and allyl bromide followed by epoxidation with pertrifluoroacetic acid. However, the reaction between fluorodinitroepoxybutane and fluorodinitroethanol always led to polymerization of the epoxide. (C)

Compound II, $\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{F}$. Numerous approaches to the synthesis of Compound II were investigated. Only one gave any degree of success. The intermediate secondary alcohol

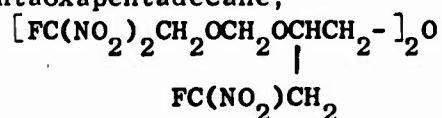


was prepared by the reaction of GFDNE with fluorodinitroethanol, but the yield was less than 1%. This and other routes were studied and found to be impractical for plasticizer synthesis. (C)

Nitrodifluoramino formals were proposed and studied since the physical properties expected of Compounds I, IA, and II could be achieved with the formals without loss of energy, and because the formals could be prepared with much less difficulty and in higher yield than the ethers. (C)

The synthesis of each of six formals proposed involved the reaction of a nitrodifluoramino alcohol with the chloromethyl ether of fluorodinitroethanol or dinitropropanol. Three of the formals were prepared but their densities were low. An observation made during the preparation of one of the formals, FYOF, led to the synthesis of the symmetrical formal, bis[5-fluoro-5,5-dinitro-2,2-bis(difluoramino)pentyl] formal, SYFO. Our preliminary tests on the compound were encouraging; therefore a sample was prepared and submitted to AFRL for further tests. Their results showed that SYFO was the best plasticizer tested to date. Because of the interest shown in SYFO, we have conducted a preliminary investigation of scale-up procedures for the preparation of pound quantities. At the present time it appears that the reactions can be scaled up to prepare several pounds of SYFO for motor firings. This work will resume in the near future. (C)

Fluoronitroethers were investigated briefly and synthesis achieved of DIAD, 1,15-difluoro-1,1,15,15-tetranitro-6,10-bis(2-fluoro-2,2-dinitroethyl)-3,5,8,11,13-pentaoxapentadecane,



This compound appears to meet all of the plasticizer requirements; however, it is not as energetic as SYFO. Additional work on DIAD was postponed in preference to work on SYFO.

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